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for January, 1936

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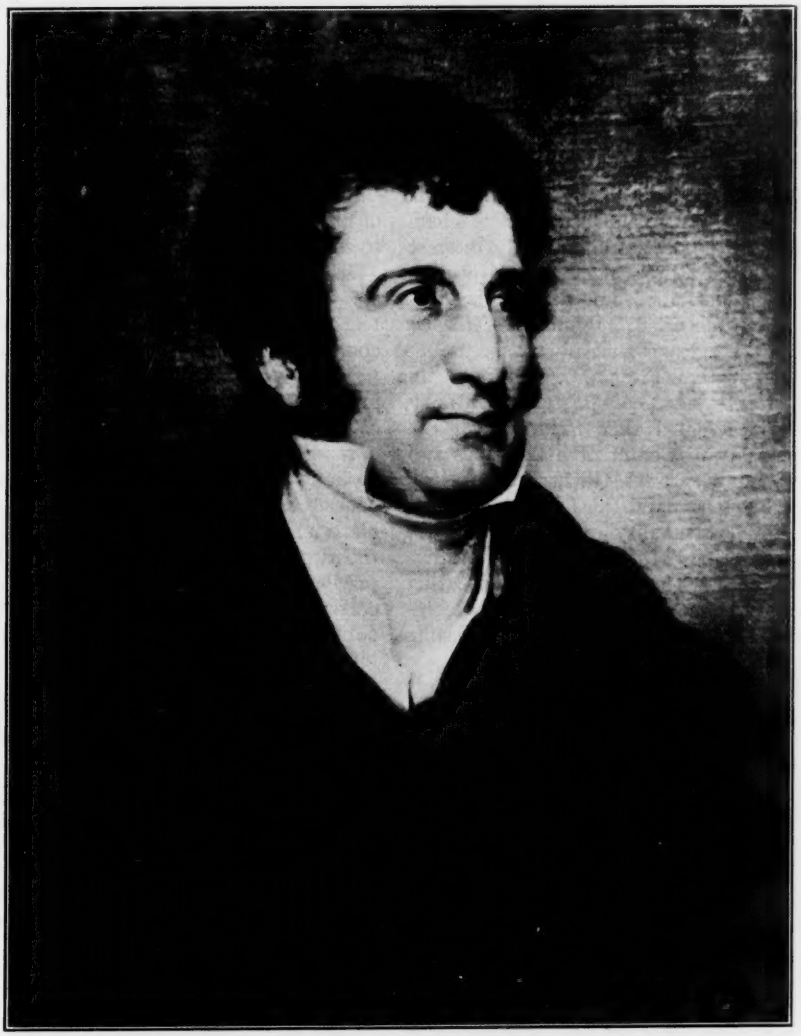

ROBERT HARE (1781–1858)

Professor of chemistry, University of Pennsylvania, 1818–1847

Reproduction of a portrait of Robert Hare, attributed to Rembrandt Peale, the original of which is in the Independence Hall National Museum, Philadelphia.

Robert Hare, at the age of twenty, gave to the world his compound blowpipe and the oxy-hydrogen flame in a paper presented to the Chemical Society of Philadelphia, the first chemical society in the world. In his colorimeter and deflagrator he provided chemists and physicists with new and powerful sources of electric energy. He was a pioneer in gas analysis. He gave us artificial graphite, pure charcoal, calcium carbide, and was the inventor of the mercury cathode. To him we owe the first electric furnace, "promptly forgotten and re-invented many years later." Dr. Bancroft has said: "If we call Moissan the Christopher Columbus of the electric furnace, we must call Hare the Leif Eriksen of the same." Dr. Doremus adds: "Another of Hare's most important contributions to general welfare was his 'rock-blasting' apparatus...where by the use of a 'plunge battery'... a wire is brought to incandescence, and thus becomes the means of igniting gun-powder, or other explosive, and this at any distance, under water, or practically any condition. As one looks around New York today and wonders at its sky-scrapers, its magnificent bridges over deepened waterways, its underground tunnels, its tunnels beneath rivers, its splendid water supply brought from the Catskills, under three rivers, and finally the Narrows to Staten Island, an engineering operation second only to the construction of the Panama Canal, how little we realize our indebtedness to Hare for his rock-blasting device." (*Contributed by the Edgar Fahs Smith Memorial Collection in the History of Chemistry, University of Pennsylvania, through the courtesy of Miss Eva V. Armstrong.*)

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EDITOR'S OUTLOOK

PREFERRED RISKS IN TEACHING. It is interesting and encouraging to note that teachers college administrators are taking a lively interest in the problems involved in the selection of prospective teachers. The November, 1935, numbers of the *Peabody Journal of Education* and *The Journal of Higher Education* both carry articles on this subject.

In the former publication, President H. L. Donovan and Dean William C. Jones, of Eastern Kentucky State Teachers College, deal very frankly with the criticism that "students who enter normal schools and teachers colleges and who elect teacher preparatory curricula in other types of institutions are, as a group, inferior in ability and personality to those who select other professions and lines of work." That this impression is not peculiar to modern critics of education they demonstrate by selected quotations. As a commentary upon its present accuracy they cite the results of two recent objective studies.

"Studies made for the Teachers College Personnel Association by Dr. J. D. Heilman, of Colorado State College of Education, since 1931 have contributed some vital data on this issue. The members of the Teachers College Personnel Association have given their entering students the same tests—a general intelligence or ability test and certain subject matter tests. The results of these examinations tend to show that scores made by prospective teachers were somewhat lower than the scores made by students who expected to enter some other profession or line of work.

"The study of college students in Pennsylvania which was made under the direction of the Carnegie Foundation showed that prospective teachers of Pennsylvania were, as a group, inferior in the abilities measured and in their high-school records to those who did not expect to teach."

Whatever doubts one may entertain regarding intelligence and ability tests and high-school records as prognostic aids in forecasting teaching success, it scarcely seems possible to reject the conclusion that our best minds are not being recruited into the teaching profession at the elementary and secondary levels at the present time. As Dean Paul V. Sangren, of Western State Teachers College, points out in *The Journal of Higher Education*, a better quality of students will probably become interested in teaching when teaching has been made more attractive. "For one thing better prospects will come into the field when the rewards of teaching deserve it. When high-school counsellors and teachers, themselves, have sufficient personal interest in and respect for their own profession, more desirable candidates will be directed into the field. Let me repeat that one of the real problems in selection of prospective teachers is to have material from which to select."

As Dean Sangren intimates, however, the complete story of the rewards of teaching is not told in terms of teachers' salary checks. Even in the face of low income, slow advancement, and rather precarious provisions for security in old age, better prospects will be attracted to the teaching profession when candidates can feel better assured that they are preparing to enter a self-respecting and generally respected professional group. If our information is correct the United States Marine Corps, with little to offer in the way of superior material inducements, but with high morale and with the most sublime group self-esteem it has ever been our privilege to observe at first hand, experiences no difficulty in recruiting its officers from the cream of the Naval Academy graduating classes. It would be interesting, though probably depressing, to observe the effect upon the Marine Corps of two decades of officer recruiting from less promising and respected sources.

Both the articles we have cited emphasize the inadequacy (or non-existence) of means of determining the teaching aptitude or forecasting the teaching success of candidates at the time of application for entrance to teacher preparatory institutions. Indeed there are no reliable objective means of quantitatively evaluating the success of the practice teacher or of the teacher in service. Other things being equal, however, it would seem a reasonable assumption that, on the average, candidates with high intelligence ratings and high records of achievement in the subject matter they aspire to teach might be considered preferred risks. If some degree of selection and limitation were attempted on the basis of these criteria there would inevitably be an improvement in the morale of the profession and probably an increase in its effectiveness.

It is a sharp commentary on the sense of responsibility displayed by some teacher-training institutions in the past that in one state (which is probably not unique in this respect) less than twenty-five per cent. of the certificated teachers available for placement (euphemism for unemployed) can be recommended. We are glad to note the apparent awakening of conscience.

The cover picture is a reproduction of Heerschop's "Alchymist mit Gehilfen," which hangs in the Dresden Art Gallery. For loan of the photograph from which our cut was prepared we are indebted to Dr. Ralph E. Oesper of the University of Cincinnati.

The MALE SEX HORMONES*

L. RUZICKA

Technische Hochschule, Zürich, Switzerland

THE designation male hormone has, until recently, been used in the singular to cover one or more chemical substances produced in the testes which ensure the development and functioning of the male sex organs and glands, as well as the appearance and maintenance of the secondary sexual characteristics and the sex instinct. Although it was discovered by Berthold as early as 1849 that implantations of cock testicles into capons would check the usual atrophy of secondary sexual characteristics, *e. g.*, of the comb, it was not until 1929 that a quantitative physiological test for the male hormone extract was devised by Koch and Gallagher. The method consists in measuring the increase in size of a capon's comb upon administration of active material. Various modifications of the method of measurement have been devised; we have used the planimetric method for the determination of comb area. One capon unit (c.u.) is that quantity of substance which, under definitely controlled conditions, produces a 20% increase in comb area.

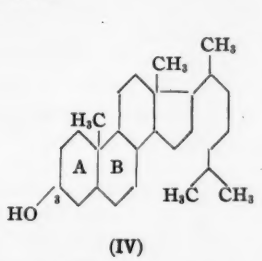
With the aid of this test Butenandt in 1931 isolated from male urine a crystalline hormone which he called androsterone. The difficulties presented by the chemical investigation of this substance may be appreciated when it is considered that until 1933 Butenandt had succeeded in obtaining only 25 mg. of androsterone. Therefore little was known of the chemical constitution and physiological properties of the compound except that it was a saturated tetracyclic hydroxyketone of the formula $C_{19}H_{30}O_2$, and highly active in the capon test.

In the meantime the knowledge of the more readily available female hormone theelin (œstrone) had reached a more advanced stage. Theelin plays in the female organism a rôle entirely analogous to that of the male hormone in the male. The female hormone test on ovariectomized mice, devised by Allen and Doisy in 1923, led to the isolation of theelin in 1929 by Doisy and, independently, by Butenandt. Theelin was recognized in 1932 as a tetracyclic ketophenol of the formula $C_{18}H_{22}O_2$.

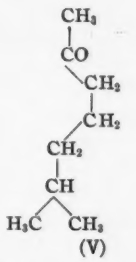
Since the sterols and bile acids were the only tetracyclic compounds previously known to occur in the animal organism it seemed possible that there might be a relationship between them and the sex hormones. The correct formula for cholesterol (I), established in 1932–33 by Wieland, Windaus, and Rosenheim and King made it feasible to investigate this possible relationship in detail. The simplest chemical relative of cholesterol which might be expected to display the chemical properties characteristic of theelin is shown in formula II.

The degradation reactions of theelin and its other chemical and physical properties as studied independently by Doisy, Marrian, Butenandt, Cook, Bernal, and others are consistent with this formulation. Indeed, formula II, proposed by Butenandt, may be regarded as definitely established, and the only question remaining is that of its stereochemical configuration.

It therefore appeared that if androsterone is also related to the sterols the composition $C_{19}H_{30}O_2$ should indicate fairly clearly the structural formula III, which represents a degradation product of a hydrogenated sterol (IV).



(IV)



(V)

Butenandt, in 1933, regarded formula III as representing a possible intermediate in the derivation of theelin from cholesterol, and in 1934 ascribed it to androsterone, which he believed to be derived from coprosterol. The possible relationship of androsterone with coprostanol was suggested to him by the fact that he had isolated pregnanediol, a compound containing the coprosterol ring system, as a by-product in the extraction of theelin from gravid urine.

Four of the 256 possible stereoisomers of the formula IV are known. Cholestanol (dihydrocholesterol) and epicholestanol both have the *trans* configuration between the rings A and B but differ in the orientation of their hydroxyl groups. Coprostanol and epicoprostanol are the corresponding *cis* isomers. In cholestanol and coprostanol the hydroxyl groups have the same orientation with respect to the ring system as a whole.

Following a process which might be analogous to the derivation of androsterone in the animal body I undertook, in 1933, with my co-workers, Goldberg, Meyer, and Brüngger, the fission of the long side-chain in the saturated sterols of the type of formula IV. Windaus had already (in 1913) isolated the side-chain cleavage product methylisohexyl ketone (V) on oxidation of cholestane with chromic acid, but had not recovered the tetracyclic ketone, $C_{19}H_{30}O$, which might be expected as the other cleavage product, and which we did in fact isolate later. To prevent oxidation of the hy-

* General Program, ninetieth meeting of the American Chemical Society, San Francisco, August 19, and meeting of the Washington, D. C., Section, A. C. S., September 4, 1935.

droxyl groups in the sterols we prepared the acetates of the four isomers mentioned and oxidized them with chromic acid, although Windaus in the same reaction with cholestanol acetate had observed only a product of the splitting of the ring A. This is probably the reason why this simple method appeared unsuitable to other workers for the preparation of degradation products containing the unchanged hydroxylated sterol ring system.

Our oxidation experiments, however, were successful, and we were able to isolate, although in very small yields, the expected four hydroxy ketones (**IV**). The isomer from epicholestanol proved to be identical with androsterone. This was very surprising because epimeric derivatives of sterols had never been detected in nature hitherto.

The subsequent application of this degradation method to the perhydro derivatives of the other well-known sterols (ergosterol, sitosterol, stigmasterol) showed that they all have the same hydroxyl position and orientation as cholesterol. On the other hand, we obtained from the bile acids the same hydroxyketone that was formed from epicoprostanol. This establishment of the configurational difference, with respect to the 3-hydroxyl group between the bile acids and the sterols, shed new light on the much-discussed relationship between the two groups of compounds and their mutual interconversion.

The preparation of androsterone from cholesterol was interesting, not only as the first artificial production and complete elucidation of a sex hormone, but as the starting point in the investigation of the relationship between chemical constitution and male hormone activity. The three stereoisomers of androsterone are all much less active than the hormone itself (c.u. = 70γ); only the derivative of cholestanol shows appreciable physiological activity (c.u. = 500γ).

The artificial production of androsterone and subsequently of other physiologically active compounds of this type facilitated extensive and thorough physiological studies. It was found that the increase in area of a capon's comb corresponds approximately to the total amount of androsterone administered and is influenced only slightly by the size and spacing of the dosage. In young chickens we were able to induce the appearance and rapid growth of the comb in the first few weeks after hatching when they would normally have no combs at all. These and supplementary studies with mature chickens demonstrated that the comb growth stimulated by androsterone is not sex-specific.

As a means of investigating the more interesting specific effect of androsterone on the accessory male glands of mammals we employed the seminal vesicle and prostate tests in castrated rats. These studies have been carried on by E. Tschopp (Basel) and by R. K. Callow and R. Deanesly (National Institute for Medical Research, London) and V. Korenchevsky (Lister Institute, London).

The atrophy of the accessory sexual glands in castrated rats is characterized not only by decrease in weight but by certain definite cytological changes. The increase in weight stimulated by androsterone is significant only when considered in combination with the cytological changes, for theelin injection also increases the weight of the gland, but results in an entirely abnormal cytological structure.

It is interesting to note (1) that small doses of androsterone are sufficient to restore an atrophied sex gland to normal morphology, (2) that somewhat larger quantities are necessary to maintain the normal weight of the glands in newly castrated mature animals, and (3) that still larger quantities are required to restore an atrophied gland to normal weight. In these tests it has been found that androsterone has a greater effect on the prostate gland than on the seminal vesicles.

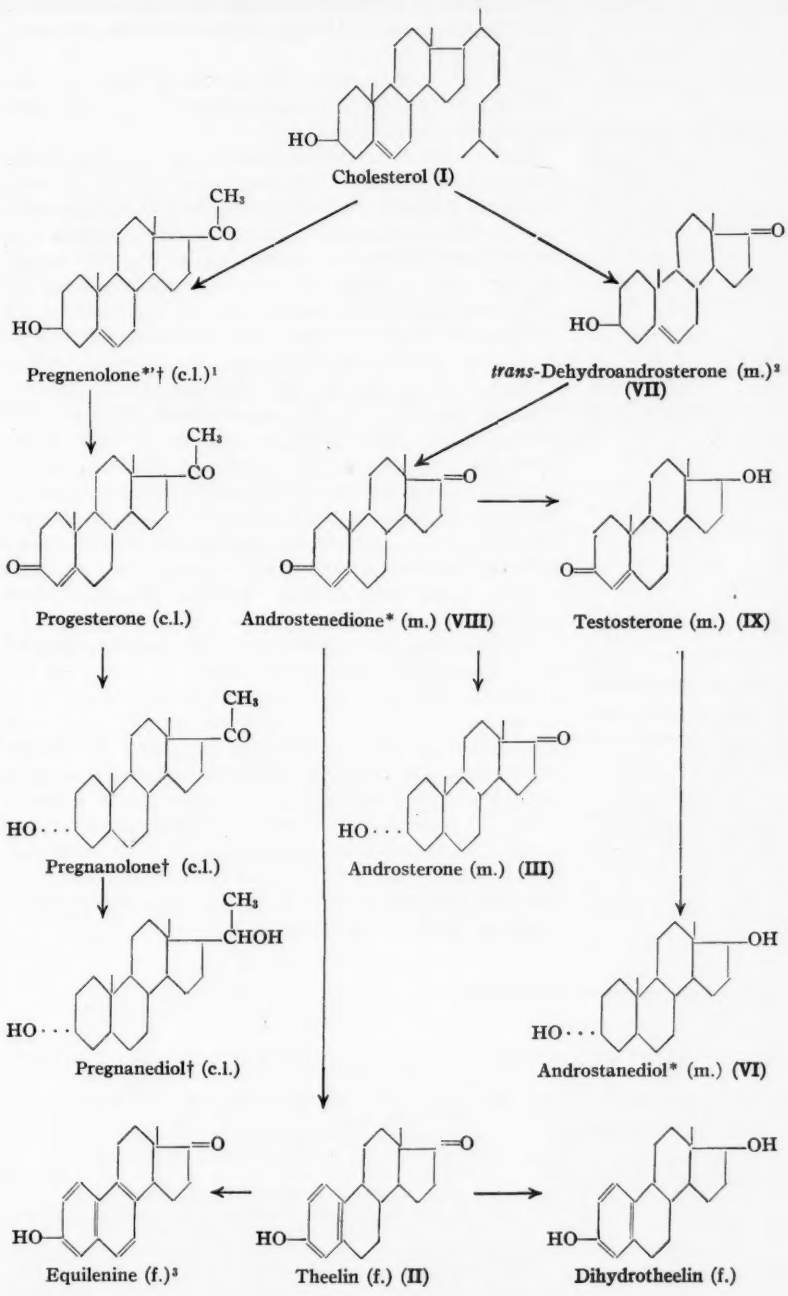
According to Korenchevsky, the physiological activity of androsterone, and of testicular extracts as well, extends to other than sex organs, which undergo various slight degenerative changes after castration.

Androsterone, the urinary sex hormone, has not been isolated from testicular extracts, although there are no marked qualitative differences in their physiological activities. However, Laqueur and co-workers, Gallagher and Koch, as well as Matzuzaki Kwanji, have observed considerable quantitative differences in the respective activities of urinary and testicular extracts. When compared in terms of capon units the testicular extracts have a considerably greater physiological effect on the sex glands of castrated rats than have the urinary extracts in general. Moreover, it has been observed that the testicular hormone activity is destroyed by alkali or permanganate, whereas the urinary extracts retain their activity after treatment with these reagents. These facts suggested that the testicular extract might contain either a synergistic substance or a hormone different from androsterone; the latter shows the same quantitative effect on accessory sex glands as the urinary extracts, from which it was isolated.

There was also to be taken into consideration the fact that highly purified testicular extracts, prepared by Gallagher and Koch, as well as by the Laqueur group, show approximately five times the potency of androsterone in the capon test. An androsterone reduction product, namely androstane-3,17-diol (**VI**) has been prepared, and displays a capon-test activity (c.u. = 15γ) which is equivalent to that of the highly purified testicular extracts. The diol, however, is even less effective in stimulating sex-gland growth in castrated rats than androsterone itself when the comparison is made on the basis of capon units.

The rat test, as well as the alkali and permanganate stability of the compound, preclude the possibility that androstanediol is the testicular hormone. Nevertheless, the qualitative similarities in the physiological activities of androsterone and its known derivatives on the one hand and the testicular extract on the other hand led us to postulate that the testicular hormone might also be chemically related to androsterone. The possible nature of this relationship is suggested by the alkali and permanganate lability of the testicular hor-

SCHEME OF THE ORIGIN OF THE SEX HORMONES



[1] Members of the corpus luteum group are indicated by (c.l.).

[2] Members of the male hormone group are indicated by (m.).

[3] Members of the female hormone group are indicated by (f.).

* These compounds have not been isolated from hormone extracts, but have been prepared artificially.

† These compounds do not show corpus luteum hormone activity.

mone activity, which tentatively indicates the presence of an α,β-unsaturated ketonic grouping. We therefore suggested in a paper published July 1 in the *Helvetica Chimica Acta* that the testicular hormone might be either androstene-3,17-dione (VIII) or androstene-3-one-17-ol (IX).

In order to prepare these compounds for physiological testing we employed a suitable variation of our usual method and oxidized the acetate of cholesterol dibromide, obtaining upon subsequent debromination and saponification androstene-3-ol-17-one (VII). This compound proved to be identical with the second urinary hormone, *trans*-dehydroandrosterone, recently isolated by Butenandt, and could be transformed by suitable oxidation procedure into androstene-3,17-dione. This compound, as evaluated by the capon test (c.u. = 100γ), is less active than androsterone, but when compared with androsterone in terms of capon units is five to ten times as effective in stimulating seminal vesicle growth in castrated rats.

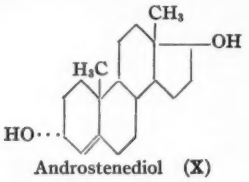
This was the first substance of known chemical constitution to exhibit the same characteristic relationship between rat-test and capon-test potency that has been established in the case of the testicular extract. It was to be expected that this observation would prove of great significance in elucidation of the constitution of the testicular hormone—an expectation which was fulfilled with surprising promptitude.

In the meantime Laqueur and co-workers described the isolation from testes of a hormone of unknown constitution which displayed a capon activity of about 10γ and which was given the name testosterone. The difference in the melting points and in the capon-test potencies of testosterone and androstenedione excluded the possibility of their identity.

Laqueur at first expressed the opinion, based on insufficient chemical evidence, that testosterone is an iso-androsterone. The characteristic physiological activity of androstene-3,17-dione in the rat test suggested

the direction that further investigation of testosterone should take. We have recently learned by private communication from Prof. Laqueur that his hormone can be oxidized to our diketone. Therefore, it appeared highly probable that testosterone is androstene-3-one-17-ol.

In pursuance of our program we, in coöperation with A. Wettstein (Ciba, Basel), reduced androstene-3-ol-17-one with sodium and alcohol to androstene-3,17-diol (**X**). The diacetate of the latter was partially saponified to the monoacetate, and the dibromide was oxidized with chromic acid. Debromination and saponification yielded synthetic testosterone, which was in all respects identical with the natural product. This preparation will make available sufficient quantities of testicular hormone for thorough physiological investigation* and possible clinical use, which have hitherto been impracticable because of the minute quantities in which the natural hormone occurs in testes.



Androstenediol (**X**)

Incidentally, the great potentialities of the simple degradation method which made possible the identification of the urinary sex hormones—androsterone and *trans*-dehydroandrosterone—are now freshly emphasized by the essential comprehension of the chemical constitution of the testicular hormone even in advance of its isolation, and by its subsequent artificial preparation.

Further investigations will reveal whether or not testosterone is in fact the most active of the compounds of male hormone activity.

The artificial preparation and the isolation from urinary and testicular extracts of unsaturated male hormones permits the formulation of a comprehensive and credible hypothesis of the origin of both male and female hormones in the animal organism. We assign the keystone position in the relationship scheme to androstene-3,17-dione, which may be regarded as an intermediate between cholesterol and *trans*-dehydroandrosterone on the one hand and testosterone, androsterone, and theelin on the other hand. In the significance ascribed to this unsaturated diketone our scheme of the origin of the sex hormones differs fundamentally from previously published systems. It is interesting to establish a complete structural parallelism between the series of the progesterone (corpus luteum hormone) group, containing twenty-one carbon atoms, and the other series, containing nineteen (male hormone group) or eighteen (female hormone group) carbon atoms.

Physiological investigations in this country supplied the quantitative tests which served as guides in the isolation and chemical investigation of the sex hormones. By international coöperation the structural elucidation of these compounds has been practically completed, and the artificial preparation of the male hormones and progesterone has made these hitherto difficultly accessible substances available for extensive study. It remains for the physiologists to determine which of the popular hopes that have been based upon the potentialities of some of the sex hormones are well founded and which are illusory.

* In the meantime it has been determined by E. TSCHOPP that the physiological activity of testicular concentrates may be attributed qualitatively and quantitatively to the action of testosterone, which is, *e. g.*, approximately fifty times as active as androsterone in terms of the rat test, and seven times as active in terms of capon units. For details consult RUZICKA AND WETTSTEIN, *Helv. chim. acta*, **18**, 1264 (1935).

AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE, SECTION C (CHEMISTRY)

St. Louis Meeting, December 30, 1935, to January 4, 1936

Wednesday afternoon, January 1, 1936 2:00 P.M.

Joint Session with Section Q (Education) and with the cooperation of the Division of Chemical Education of the American Chemical Society.

THE TEACHING OF CHEMISTRY

Ross A. Baker, *Chairman*

This is the second of a series of three symposia on the general relationships between the science of chemistry and education.

(1) The Objectives of the Subject of Chemistry 10 min.
Ross A. Baker, The College of the City of New York

(2) Teaching Chemistry for Its Cultural and Training Values 25 min.
J. H. Simons, The Pennsylvania State College

(3) Teaching Chemistry for Its Prerequisite and Professional Values 25 min.
J. C. Bailar, The University of Illinois

(4) The Problem of the Laboratory and Lecture Demonstration 20 min.
H. G. Deming, The University of Nebraska

(5) Keeping Chemistry Teaching and the Textbooks Modern 25 min.
W. D. Harkins, The University of Chicago

(6) Special Problems in the Teaching of Chemistry 25 min.
Warren C. Johnson, The University of Chicago

Thursday morning, January 2, 1936 10:00 A.M.
Session for contributed papers.

Thursday afternoon, January 2, 1936 2:00 P.M.
Session for contributed papers.

Thursday evening, January 2, 1936 6:00 P.M.
Dinner meeting arranged by the St. Louis Section of the American Chemical Society.

Thursday evening, January 2, 1936 8:00 P.M.
Evening session held jointly with the St. Louis Section of the American Chemical Society.

Address of the Retiring Vice-president, Joel H. Hildebrand, The University of California, "Dipole Attraction and Hydrogen Bond Formation in Their Relation to Solubility."

The ELECTRON *in* ORGANIC CHEMISTRY*

IV. MONOHYDROXY COMPOUNDS†

M. S. KHARASCH, OTTO REINMUTH, AND F. R. MAYO‡

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GEOMETRY AND CHEMISTRY OF ORGANIC COMPOUNDS

IN THE preceding articles of this series (*1*) we have stressed the need for a unifying concept in organic chemistry—a concept which can be employed to correlate and predict the *chemical* behavior of organic compounds. In the present-day extended Kekulé-van't Hoff-Le Bel hypothesis of molecular structure and its appropriate notation we have such a coördinating agency for the gross *geometry* of organic compounds. So unqualified has been the success of this hypothesis, within its proper field, and so convenient a basis has it formed for the classification and indexing of empirical facts that organic chemists in general have been inclined to lose sight of its intrinsic limitations and to impose upon it burdens which it was never designed to bear. In the present paper we desire to illustrate and emphasize the neglected truth that *geometrical* classifications constitute unsatisfactory bases for *chemical* generalizations. The miscegenetic union of geometry and chemistry can produce at best only empirical issue.

By the *geometry* of organic compounds we mean merely that portion of the science of which a representation may be developed by the manipulation of a set of ball-and-peg models in accordance with the ordinary valence rules. It is possible to formulate that geometry in terms of a brief list of axioms and permissible operations, but for our present purpose it is unnecessary to do so.

Such a geometry is exceedingly useful and the authors do not wish to appear to minimize its importance. We may feel confidently assured that with very few exceptions** indeed the attempt to effect laboratory operations for which no corresponding geometrical operations can be found is futile. On the other hand, even the veriest tyro in organic chemistry knows that the geometry of organic compounds is in one sense more extensive than the chemistry of organic compounds. That is to say, that a complete one-to-one correspondence cannot be established between legitimate geometrical operations and laboratory operations, nor between legitimate geometrical structures and chemical compounds. The geometrical operation, HCl + *i*-PrOH $\longrightarrow$ *i*-PrCl + H_2O, has its laboratory correspondent, but the analogous operation, HCl + PhOH $\longrightarrow$ PhCl + H_2O, has not. Trihydroxy carbinol is a respectable geometrical structure, but it is to chemistry what hen's teeth are to poultry husbandry, or what blue dahlias are to horticulture.

The student who has mastered the *geometry* of organic compounds has made a necessary beginning, but his condition is analogous to that of the beginner at chess who has learned the names and moves of the pieces and the rules of the game. The game itself (*i. e.*, the *chemistry* of organic compounds) he has still to learn.

As the student's knowledge and experience increase he gradually acquires the ability to differentiate between those geometrical operations which have, or are likely to have, laboratory correspondents and those which have not or probably have not. He may maintain that he has acquired the ability to read chemistry out of his geometry, but in so maintaining he shows that he has not critically examined his own mental processes. Actually, he is merely associating an extrapolation of his chemical knowledge and experience with his geometry.

That which underlies the differentiation between geometrical operations that have and those that have not laboratory correspondents we have chosen to call the *chemistry* of organic compounds. Together, geometry as we have defined it and chemistry as we have defined it go to make up what is commonly known as the science (and/or art) of organic chemistry.

In so far as the organic chemist's intellectual equipment, in addition to his organic geometry, consists in empirical knowledge and a facility for entertaining sound "hunches," his vocation is an art rather than a science. In this sense many of our ablest and most successful organic chemists are artists rather than scientists.

The authors believe, however, that much of the present art of organic chemistry may be so systematized and rationalized as to transfer it into the field of true science. The first necessary step is the abandonment of efforts

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* Numbers I, II, and III of this series appeared in J. CHEM. EDUC., **5**, 404–18 (Apr., 1928); **8**, 1703–48 (Sept., 1931); and **11**, 82–96 (Feb., 1934), respectively.

† Contribution from the George Herbert Jones Laboratory of The University of Chicago.

‡ Present location, E. I. du Pont de Nemours & Co., Wilmington, Delaware.

** The preparation of the triarylmethyl free radicals might be regarded as an "exception" since it violates the quadrivalency rule.

to establish a non-existent correspondence between *geometrical* classifications of compounds and *chemical* generalizations concerning properties. The second is the adoption of a notation to which one may assign *chemical* as well as *geometrical* implications.

THE CLASSICAL TREATMENT OF ALCOHOLS

The chemistry of the alcohols furnishes an unusually apt illustration of our thesis, for in this field the geometrical-chemical generalizations which we criticize are numerous and widely current. Moreover, the underlying reasons for their validity, in so far as they are valid, the limits of their applicability, and the reasons for the exceptions to them, are all readily ascertainable —indeed obvious—in the light of the theory set forth by the authors in previous articles of this series.

Kolbe's (*2*) classification of alcohols as primary, secondary, and tertiary was suggested by differences in the behavior of isomeric aliphatic alcohols, notably the differences specified in his oxidation rule. Yet on closer examination Kolbe's oxidation rule proves to be a pure geometrical proposition rather than a chemical generalization linked to a geometrical classification. The rule states in effect that, when a specified operation is performed upon two given geometrical structures, two other respectively corresponding geometrical structures must result, and it adds that a third given structure is debarred by its geometry from undergoing the specified operation. The fact that the geometrical operations involved have laboratory correspondents should not becloud the issue.

Analogous to Kolbe's rule in this respect is Ipatiew's (*3*) generalization that, when passed through glowing tubes, primary alcohols yield aldehydes, secondary alcohols yield ketones, and tertiary alcohols yield olefins.

Nevertheless Kolbe's rule seems to have been generally accepted as a precedent for the formulation of the hybrid rules which the present authors deplore. Some illustrative examples of the geometrical-chemical rule follow.

* * *

"Secondary alcohols are oxidized more readily [by permanganate] than the primary. Lengthening the chain, the introduction of phenyl or a double linkage increases the reaction velocity" (*4*).

"Tertiary alcohols, which dehydrate easily, forming unsaturated hydrocarbons, are thus decomposed into two molecules at the boiling point of naphthalene (218°), while primary and secondary alcohols remain intact. However, if the temperature be raised to 360°, the boiling point of anthracene, the primary alcohols alone resist; the secondary and tertiary are decomposed" (*5*).

"The primary fatty alcohols are not converted into chlorides by hydrochloric acid [*i. e.*, by distilling mixtures of alcohol and conc. aq. acid]. Some secondary alcohols are so converted at slightly elevated temperatures, while tertiary alcohols react with this reagent at room temperatures" (*6*).

"Phthalic anhydride combines completely with a primary alcohol in an hour or two at 80° but requires several hours at 140° with a secondary alcohol. At this temperature it dehydrates a tertiary alcohol instead of combining with it . . ." (*7*).

"The initial rate of esterification of primary alcohols with acetic acid or acetic anhydride is greater than that of secondary alcohols, which is in turn greater than that of tertiary alcohols" (*8*).

* * *

The reader will note that all the foregoing statements are fairly reliable so long as their application is confined strictly to saturated aliphatic alcohols. As soon as we overstep this limited field, however, anomalies begin to spring up. Indeed, even within the circumscribed field of aliphatic alcohols we encounter the warning that, "Statements . . . contrasting classes of alcohols must be considered as applying to the average of the class since there is considerable variation within each class, some secondary alcohols being as reactive as some primary and some tertiary approaching some secondary" (*9*).

Unfortunately, systematic investigations of the chemical properties of the alcohols have been rare. The few available are of limited extent and most of them are open, in part at least, to criticisms, some of which we shall point out. For the most part the correlator must content himself with widely scattered observations and experiments, extremely few of which are mutually comparable. Many of the data recorded in the literature relate to impure specimens treated with impure reagents under ill-controlled conditions. *In short, the vast, miscellaneous collection of facts, near-facts, and irrelevancies which constitutes our present knowledge of the chemical properties of the alcohols furnishes as cogent a demonstration of the need for a guiding principle in fundamental organic research as any the authors could offer.* It follows that no unified general treatment of the chemical properties of the alcohols can be completely substantiated by experimental facts at the present time. Nevertheless, we believe that the general outlines of the picture are discernible and that they conform very closely to the sketch which the theories previously set forth by the authors would suggest.

Let us begin by taking note of a few questions upon which a unified theory should shed some light. Why do the phenols and naphthols exhibit practically none of the chemical characteristics of the tertiary alcohols with which they would naturally be classed geometrically? Why do benzyl and allyl alcohols—both primary alcohols—behave in most respects like secondary aliphatic alcohols? Why do the diaryl carbinols resemble the tertiary aliphatic alcohols much more strongly than they resemble the secondary aliphatic alcohols to which they are geometrically analogous? Why are the characteristics of the triaryl carbinols such that they are ordinarily regarded as belonging in a class by themselves? In short, what is the underlying cause of the vast chemical differences between individual alcohols?

SOME ASPECTS OF THE ELECTRONIC CONFIGURATION OF MONOHYDROXY ORGANIC COMPOUNDS

The first step toward arriving at satisfactory answers to these questions consists in discarding all previous *formal* classifications of alcohols. Let us go even far-

ther and agree to regard all monohydroxy organic compounds as representatives of a single type, ROH. When this is done it is possible, as the authors undertake to demonstrate, to arrange the individual representatives of the type in a series such that no abrupt transitions of chemical properties occur between one member and the next. The aggregate change in properties from one end of our series to the other is tremendous, yet consideration of the series as a whole reveals that the differences we observe are differences of *degree* rather than of *kind*.

Our general chemical knowledge would lead us to characterize all organic compounds of the type ROH as distinctly polar. In terms of the authors' notation the electron-pair constituting the R-to-hydroxyl bond is displaced away from the radical R and toward the hydroxyl group. The considerable range of relative electronegativities among organic radicals would also suggest, however, that the actual degree of relative displacement of the bonding electron-pair should vary from compound to compound. This idea is set forth graphically in Figures 1 and 2.

The order of arrangement we propose to follow in compiling our representative series of ROH compounds is the order of relative electronegativity of the respective radicals R. This order and the means of determining it have been discussed *in extenso* in earlier articles of this series (*1*, *a*, *c*) and elsewhere (*10*). For convenience in reference we append the following list of radicals in descending order of relative electronegativity: *p*-anisyl > *o*-anisyl > α-naphthyl > *o*-tolyl > *p*-tolyl > *m*-tolyl > phenyl > *p*-chlorophenyl > *o*-chlorophenyl > *m*-chlorophenyl > 2,4-dichlorophenyl > 2,5-dichlorophenyl > methyl > ethyl > *n*-propyl > *n*-butyl > *n*-heptyl > *i*-propyl > benzyl > β-phenylethyl > *p*-chlorobenzyl > *o*-chlorobenzyl > *m*-chlorobenzyl > tert.-butyl > diphenylmethyl > triphenylmethyl.

The relative electronegativities of all the foregoing radicals have been determined experimentally. On the basis of miscellaneous but extensive chemical evidence various other radicals may be tentatively placed in the series. Thus, *sec.*-butyl probably belongs just above *i*-propyl, and *sec.*-amyl just above *sec.*-butyl. Allyl belongs near (and probably slightly below) benzyl. The tolylmethyl radicals belong below the benzyl radical, with α-naphthylmethyl below them and the anisylmethyl radicals still lower. The di- and tritolylmethyl and the di- and trianisylmethyl radicals would be correspondingly related to the diphenylmethyl and triphenylmethyl radicals, respectively.

HALIDE FORMATION

Under proper experimental conditions bonds of type 2 as exemplified in Figure 1 are, in general, susceptible to polar scission.

$$A\text{———}:\text{—}B \longrightarrow A^+ + :B^-$$

The degree of susceptibility naturally varies with the identities of the constituents A and B, and diminishes as the bond approaches the conformation illustrated in type 1, Figure 1.

(1) A—:—B
(2) A———:—B
(3) A———:———B

FIGURE 1.—PRINCIPAL TYPES OF COVALENT BONDS
Type (2) is representative of R-to-OH bonds in general

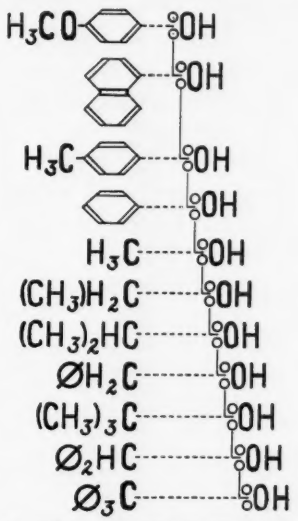


FIGURE 2.—QUALITATIVE REPRESENTATION OF SOME TYPICAL R-TO-OH BONDS

These considerations immediately suggest the possibility of the chemical substitution of some other electronegative unit or units for the hydroxyl radical in compounds of the ROH class. By reason of the comparative wealth of experimental data available the reactions of alcohols with halogen acids constitute an excellent medium for the examination of this kind of chemical transformation. In Table 1 we list a representative selection of ROH compounds arranged in the order of decreasing electronegativity of the radical R.

Here the reader will note that it is possible to assign an appropriate place to any ROH compound whatsoever, provided only that the relative electronegativity of its radical R can be experimentally determined or logically estimated. Geometrical structure is not the basis of arrangement and the rules relating to primary, secondary, and tertiary aliphatic alcohols appear as superficial, empirical generalizations of very limited applicability.

It is interesting to consider the data abstracted in Table 1 in connection with the probable mechanism of the alcohol-halogen acid reaction. The authors, however, wish to emphasize the fact that the mechanism postulated is not an essential part of their theory. The significant fact that the relative reactivity of an alcohol toward halogen acids may be correlated with the relative electronegativity of the constituent alcoholic radical R remains, regardless of the mechanism of reaction.

The authors recognize that highly plausible reaction mechanisms are sometimes shown to be impossible in the light of increasing knowledge. On the other hand, a complete disregard for reaction mechanisms too often leads to the drawing of unwarranted conclusions from comparisons between reactions that are fundamentally different and hence incomparable.* On the whole, restrained and reasonable speculation upon reaction mechanisms is, more often than not, stimulating and instructive.

TABLE 1

REPRESENTATIVE REACTIONS OF SOME TYPICAL MONOHYDROXY COMPOUNDS WITH HALOGEN ACIDS

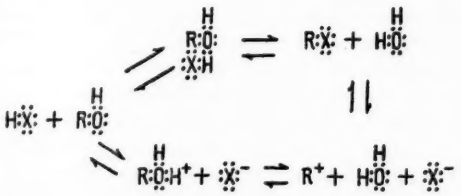
Phenol	Unaffected by halogen acids.
Methanol	MeOH + HI (g.) $\xrightarrow{0\text{–}4°C.}$ MeI (quantitatively) (*29*). MeOH + HBr (sp. gr., 1.49) $\xrightarrow{\text{Slow dist.}}$ MeBr (50% yield) (*29*). MeOH + HCl (g.) + $ZnCl_2$ $\xrightarrow{\text{Boiling}}$ MeCl (*70*).
Ethanol	EtOH + HI (sp. gr., 1.7) $\xrightarrow{\text{Dist.}}$ EtI (*71*). See also (*6, 29*). EtOH sat. with HBr (g.) $\xrightarrow{70\text{–}80°C.}$ EtBr (*72*). See also (*6*). EtOH sat. with HCl (g.) $\xrightarrow{100°C.}$ EtCl (12 hrs., 93% yield) (*70*). $\xrightarrow{\text{Sealed tube}}$ See also (*73, 74, 75, 76*).
n-Propanol	*n*-PrOH + HI (sp. gr., 1.7) $\xrightarrow{\text{Dist.}}$ *n*-PrI (*6*). See also (*29, 80*). *n*-PrOH + HBr (sp. gr., 1.49) $\xrightarrow{\text{Dist.}}$ *n*-PrBr (*6*). See also (*72*). *n*-PrOH distilled with aq. HCl (dil. or conc.) yields no chloride (*6*). *n*-PrOH sat. with HCl (g.) and distilled after long standing yields *n*-PrCl (*78*). See also (*79*).
sec.-Butanol	MeEtCHOH + HI (sp. gr., 1.7) $\xrightarrow{\text{Dist.}}$ MeEtCHI (*6*) MeEtCHOH + HBr (sp. gr., 1.49) $\xrightarrow{\text{Dist.}}$ MeEtCHBr. (*6*). See also (*81*). MeEtCHOH + large excess HCl (sp. gr., 1.10) ⟶ MeEtCHCl (*6*). See also (*82, 83*).
i-Propanol	*i*-PrOH + HI (sp. gr., 1.7) $\xrightarrow{\text{Dist.}}$ *i*-PrI (*6*). See also (*29, 77, 80*). *i*-PrOH + HBr (sp. gr., 1.49) $\xrightarrow{\text{Dist.}}$ *i*-PrBr (*6*). See also (*72, 77*). Equimolecular mixture of *i*-PrOH and conc. aq. HCl, saturated with HCl (g.) and heated 6–8 hrs. at 150°C. gives *i*-PrCl (yield not stated) (*77*).
Phenylcarbinol	$\text{Ø}CH_2OH$ + HCl (g.) ⟶ $\text{Ø}CH_2Cl$ with evolution of heat (*84*). $\text{Ø}CH_2OH$ + HCl (sp. gr., 1.12) $\xrightarrow{\text{Warmed}}$ $\text{Ø}CH_2Cl$ (*6*).
Trimethylcarbinol	Me_3COH + HCl (g.) $\xrightarrow{\text{Room temp.}}$ Me_3CCl (*79*). See also (*85*). Me_3COH + HCl (conc. aq.) $\xrightarrow{\text{Room temp.}}$ Me_3CCl (*6*).
Diphenylcarbinol	Ø_2CHOH (benzene soln.) + HCl (g.) ⟶ Ø_2CHCl (*86*). See also (*87*).
Triphenylcarbinol	Ø_3COH (benzene soln.) + HCl (g.) ⟶ Ø_3CCl (*88*). See also (*89, 90*).

Formally, the reaction of a halogen acid with an alcohol resembles one type of acid-base neutralization. However, it is the superficiality of this resemblance rather than the resemblance itself that should be emphasized. Some textbooks do, indeed, point out that the combination of hydrogen with hydroxyl ions is immeasurably rapid, whereas the reaction of an alcohol with a halogen acid is often very slow, and conclude on this basis that the two reactions must differ in nature.

In accordance with modern electrolytic theories, the interaction of HCl with NaOH in aqueous solution is represented as follows:

$$H_3O^+ + Cl^- + Na^+ + OH^- \rightleftharpoons 2H_2O + Na^+ + Cl^-$$

The authors believe that the probable mechanism of the interaction of a halogen acid with an alcohol should be summarized in a different way:



The equation as written does not take into account everything that may happen; further possibilities will be discussed in connection with etherification.

At this point it is pertinent to recall the general rule that the order of decreasing reactivity of halogen acids with alcohols is hydriodic, hydrobromic, hydrochloric. This is the order of reactivity that has been observed with respect to the addition of halogen acids to olefins, and which has been discussed in detail in the second article of this series (*1b*, pp. 1729–31). Indeed, it is altogether possible that the entities involved in the two cases are identical. If we designate by R′ the olefin corresponding to a given radical R, the first stage in the addition of a halogen acid to the olefin might be postulated as:

$$R' + H^+ \rightarrow R^+$$

In order to combine with a halide ion the R^+ ion must acquire a sharing interest in a pair of the halide-ion valence electrons. The iodide ion, of course, yields electrons more readily than the bromide ion, which in turn yields them more readily than the chloride ion.

Let us now inquire what effects the relative electronegativities of divers radicals R might be expected to have upon the mode of dissociation of the simplest possible intermediate complex which may be postulated as taking part in halide formation. If we consider the complex ion ROH_2^+ one effect immediately suggests itself. When R is strongly electronegative we would be inclined to represent the probable dissociation of the complex as follows:†

* For an illustrative example, see the footnote beginning on p. 84 of the third article of this series (*1c*).

† We are well aware that the presence of lone protons in solution is highly improbable. In the equations employed it is merely our desire to center attention upon the essentials of the discussion and avoid side issues; hence we leave the protons to take care of themselves. For the same reason other ions, molecules, and complexes present in the experimental system are ignored.

$$R^+ + H_2O \rightleftharpoons ROH_2^+ \rightleftharpoons ROH + H^+$$

When R is less electronegative—say comparable in electronegativity to hydrogen—our equation might be written as follows:

$$R^+ + H_2O \rightleftharpoons ROH_2^+ \rightleftharpoons ROH + H^+$$

When R is very weakly electronegative—definitely less electronegative than hydrogen—we would reverse the emphasis in our first equation and write:

$$R^+ + H_2O \rightleftharpoons ROH_2^+ \rightleftharpoons ROH + H^+$$

Hence one would predict that the R^+ ions most readily formed would be those corresponding to the least electronegative R radicals. Moreover, the R^+ ions more readily formed are also the ones which should react more readily with halide ions, since they are the more susceptible to reduction in that they can share electrons in energy levels farther removed from the nucleus, and hence need oxidize the halide ions with which they combine to a lesser degree. These expectations are in good agreement with the data abstracted in Table 1.

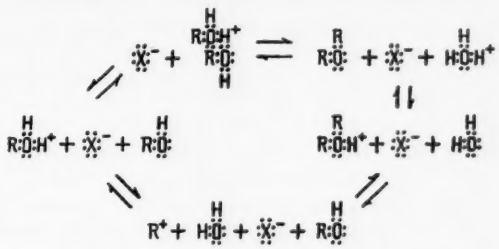
Since, in addition of halogen acids to olefins and in the reaction of halogen acids with alcohols, we are probably dealing in part with identical processes it is not surprising to find a direct correlation between ease of reaction and instability of reaction product in both cases. Thus, only the slightest trace of phenol is obtained by treating phenylchloride with water in an autoclave at 300° for ten to twenty hours (*11*). Methyl and ethyl chloride are both well known to be fairly resistant to hydrolysis by means of water alone. Tertiary butyl chloride, however, is almost completely converted to the alcohol by heating in a sealed tube with three or four volumes of water on a water bath for ten hours. The same reaction proceeds at an appreciable rate at room temperature (*12*). Triphenylmethyl chloride is slowly hydrolyzed in contact with cold water, and immediately by hot water (*13*). Indeed, so susceptible to solvolysis is this chloride that upon heating it in benzene solution with methyl alcohol (*14*) or with ethyl alcohol alone (*13*) one obtains practically quantitative yields of the unsymmetrical ethers.

ETHERIFICATION

There is sufficient relationship between halide formation and etherification to invite simultaneous consideration of the two.

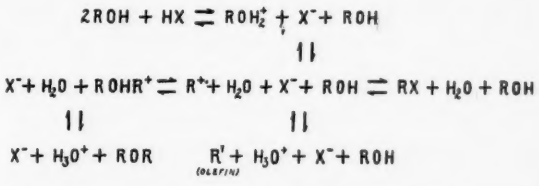
The almost universal promulgation in textbooks of organic chemistry of Williamson's (*15*) mechanism for the etherification of ethyl alcohol has tended to obscure the fact (at least for students) that intermediate sulfate formation is not essential to etherification. Van Alphen (*16*) has emphasized this fact and has invited attention to the generality of the proton-catalyzed reversible reaction involving ether-formation. He points out that etherification takes place under many conditions which do not necessitate the postulation of intermediate "salt" formation and in some cases where this mechanism seems highly improbable, if not impossible. Indeed, it is worth remarking that even in Williamson's preparation of diethyl ether, the formation of ethyl hydrogen sulfate may be merely a coincidence rather than a significant stage in the reaction. It is not at all unreasonable to interpret the interaction of ethyl hydrogen sulfate with ethyl alcohol to yield ether as a special case of the etherification of alcohol in the presence of a fairly strong acid.

The present authors would represent the mechanism of the general etherification reaction as follows:



The resemblance to halide formation is obvious and the relationship is further emphasized by Reynoso's (*17*) observation that a mixture of aqueous hydrochloric acid and ethyl alcohol heated in a sealed tube at 100° yields (aside from unchanged alcohol) ethyl chloride and ether. He further noted that the yield of ether, as compared with ethyl chloride, is relatively low when the HCl content of the reaction mixture is high, and increases with dilution of HCl. Higher temperatures also favor higher ether yields. However, when the temperature is raised sufficiently we find the positive ethyl ion (or its corresponding complex) unstable, and ethylene is among the products of the reaction.

With due regard for the facts that for certain alcohols olefin formation is impossible and that for others some of the reactions represented may prove irreversible at temperatures at which other reactions take place we might write, in general, the following series of interrelated equilibria:*



From this scheme it is evident why too high a concentration of acid should be avoided when an ether is the desired product, unless the alcohol and acid employed are such that their "acidate" is very susceptible to alcoholysis. We have already noted this susceptibility in the case of triphenylmethyl chloride:

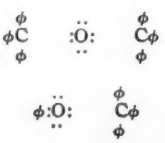
* For convenience in summarization we have employed a simple ionic formulation here.

$$\phi_3CCl + HOEt \longrightarrow \phi_3COEt + HCl$$

So far as self-etherification is concerned we might expect to find that the alcohols in which R is strongly electronegative would undergo polar scission of the R—OH bond less readily and hence would etherify with greater difficulty (see equation, p. 11). In general this is true. Phenol undergoes self-etherification only in the presence of such powerful condensing agents as $AlCl_3$. Ethyl alcohol is slowly converted into diethyl ether by aqueous HCl at water-bath temperature (*17*). As we approach the bottom of Figure 2, however, the picture changes and we find that benzhydrol, unless carefully freed of all traces of acid or halide, cannot be distilled or even heated without etherification (*18*). Indeed it has been reported that this alcohol etherifies merely on distillation (*19*) and, stranger still, upon refluxing with water (*20*), but these observations are most likely attributable to insufficient purification. It may be true as reported that triphenyl carbinol (*14*) is sufficiently susceptible to etherification to form an unsymmetrical ether with methyl alcohol without the addition of acid, though it is possible that acid contamination plays a part here also.

What we have just said should not be taken to imply that under practical laboratory conditions the yields from acid-catalyzed self-etherifications will increase uniformly (or will be obtained in progressively shorter times) as we proceed downward through our table of representative alcohols. Two factors interfere with such a smooth progression. The first is found in the relative thermal stabilities of the R^+ ions. Tertiary butyl alcohol furnishes a striking illustration. Me_3C^+ ions should be formed much more readily and in much greater numbers than Me^+ or Et^+ ions and doubtless they are. Their thermal stability is so low, however, that under the conditions usually imposed they immediately eliminate protons and are converted into isobutylene molecules.

The second interfering factor is the susceptibility of the resultant ether to acid scission or hydrolysis. We might expect ethers containing two very weakly electronegative radicals, or one very weakly electronegative and one very strongly electronegative radical to be highly susceptible to acid hydrolysis. As a matter of fact, both triphenylmethyl oxide (*21*) and phenyltriphenylmethyl ether (*22*)



are unstable in the presence of dilute acids even. Here again the correlation of ease of reaction with low stability of the reaction product holds good, with the qualification that ethers as a class are considerably more resistant to hydrolysis than are halides as a class.

It follows from the foregoing discussion that, within the range permitted by the acid stability of the products, and with the exceptions excluded by the thermal instability of the intermediate ions, one might expect alcohols in which the radical R is strongly electronegative to etherify rather readily with alcohols in which the radical R is very weakly electronegative, the latter furnishing the positive R^+ ions. This is in accord with the available data.

An additional complication arises, however, when the attempt is made to etherify phenols with triaryl carbinols, because of the well-known reactivity of the *para* hydrogen atoms in benzene derivatives of this type. Treatment of triphenylcarbinol in glacial acetic acid with phenol and H_2SO_4 (*23*), or fusion of the carbinol with phenol (*24*) leads, not to etherification, but to formation of *p*-hydroxytetraphenylmethane.

The same product results when phenol and the carbinol are warmed in benzene solution. Indeed phenyltriphenylmethyl ether, in the presence of free phenol, rearranges at water-bath temperature; the same rearrangement takes place slowly at room temperature in benzene solution of the ether to which a little phenol has been added (*25*). It is highly probable, in view of the method of preparation employed and the melting point reported for the product, that the "phenyl ether" of di-α-naphthylcarbinol reported by Schmidlin and Massini (*26*) is actually a compound of the *p*-hydroxyphenylmethane type.

That phenol is capable of undergoing a normal etherification reaction may be demonstrated if we fulfil the necessary conditions (1) that the other alcohol employed be capable of losing its hydroxyl group readily enough to furnish some (fairly stable) positive ions, but not readily enough to form a *p*-hydroxyphenol condensation product, and (2) that the acid catalyst employed be fairly strong, reasonably non-volatile, incapable of substituting the phenol ring, and incapable of forming a product (stable under the conditions of the experiment) with the other alcohol. These conditions are only partially fulfilled when phenol and methanol are treated with concentrated H_2SO_4, although a low yield of anisol may be obtained in this way (*27*). They are better satisfied by the process for the preparation of anisol and phenetol employing naphthylsulfonic acid (*28*).

DEHYDRATION AND PYROLYSIS

Etherification may, of course, be regarded as an intermolecular dehydration. It is interesting to extend the principles already discussed in connection with etherification to a consideration of intramolecular dehydration. We have already noted that such dehydration may be initiated by the acid-catalyzed mechanism which plays a part in etherification. Whatever may be the mechanistic details of other diverse homogeneous and heterogeneous reactions resulting in alcohol

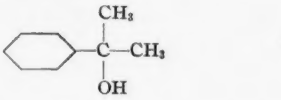
dehydration, it is probable that most of these reactions consist essentially in the abstraction of an hydroxyl ion from the molecule with subsequent or simultaneous elimination of a proton from the residual organic ion, which is unstable under the prevailing experimental conditions.

If this hypothesis be valid the susceptibility to dehydration of an alcohol, ROH, must be inversely related to: (1) the electronegativity of the radical, R, and (2) the stability of the ion R^+ (with respect to proton elimination). The influence of temperature upon both of these determinants is obvious.

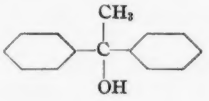
A rapid survey will serve quite as well as an exhaustive and tedious review to indicate the trend of the experimental data. The naphthols and phenols contain strongly held hydroxyl groups and are singularly resistant to intramolecular dehydration. Indeed they appear to withstand heat treatment until the ring structures themselves begin to disintegrate (*30*). Methanol should, perhaps, be regarded as a special case on the ground that all its hydrogen atoms are directly attached to the carbinol carbon atom. The high ratio of CO + CO_2 to H_2O in its pyrolysis products (*31*), however, tends to confirm our belief that the C—OH bond is not very readily broken. That ethyl alcohol is dehydrated to yield ethylene rather than ether in the presence of an excess of hot concentrated acid, many a student of elementary organic chemistry learns to his sorrow in the laboratory. Not only ethyl alcohol, but other primary aliphatic alcohols are converted to olefins when passed in the vapor state over acid or readily hydrolyzable salts at temperatures near 300°C. or lower, depending upon the individual salt employed (*32, 33, 34*). We have already cited the observations of Kling and Viard (*5*) regarding the dehydration of secondary and tertiary aliphatic alcohols upon heating.

The aryl carbinols, such as benzyl alcohol and benzhydrol, may again be regarded as special cases, since the only hydrogen atoms they contain (other than the strongly held ones of the phenyl nuclei) are attached directly to the carbinol carbon atoms. Their intermolecular dehydrations, however, are indicative of the respective stabilities of their C—OH bonds. Benzyl alcohol, maintained under pressure slightly above its boiling point for five days, is almost completely converted into dibenzyl ether and the thermal decomposition products thereof, chiefly toluene and benzaldehyde (*35*).* We have already noted that benzhydrol must be carefully freed of acid impurities if it is to escape considerable etherification on distillation.

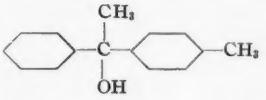
Methylphenylcarbinol, however, yields styrene when heated with 3 to 5% $KHSO_4$ (*36*). As further representative of the normal intramolecular dehydration of aryl carbinols we tabulate the following data collected by Hurd (*37*). We have arranged the carbinols in the order of decreasing electronegativity of their radicals.



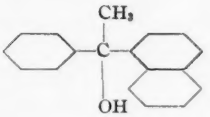
Four distillations give 53% yield of β-phenylpropylene.



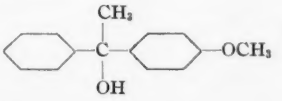
Three distillations give 58% yield of unsymmetrical diphenylethylene.



"Best dehydrated by three distillations at atmospheric pressure."

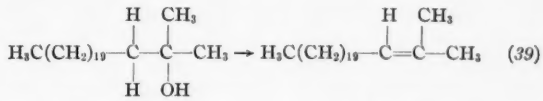


Dehydrated to corresponding ethylene by one distillation at diminished pressure.

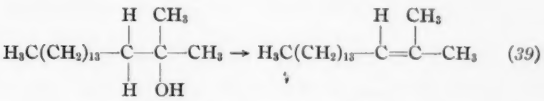


Dehydrated to corresponding ethylene by one distillation at diminished pressure.

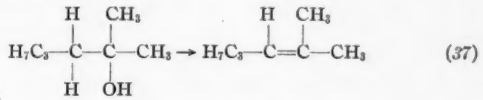
Several further examples may be of incidental interest as illustrating the tendency, when there are two hydrogen-bearing carbon atoms adjacent to the carbinol carbon atom, for hydrogen elimination to take place at the less electronegative one. We do not wish to emphasize this point unduly in view of the fact that dehydration of the more complicated aryl carbinols is often accompanied by molecular rearrangement (*38*); in the instances cited, however, rearrangement scarcely seems probable.



(*39*)



(*39*)



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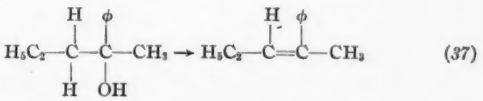

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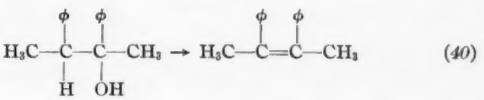


(*40*)

In the preceding article of this series (*1c*, p. 87) we

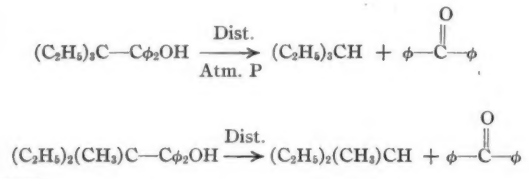
* The benzaldehyde might be attributed to a dehydrogenation reaction, except that it occurs in almost equimolecular quantities with the toluene, as is the case when pure dibenzyl ether is decomposed under the same conditions, and that there is no appreciable pressure when the cooled tube is opened. One would scarcely postulate complete utilization of hydrogen in the hydrogenation of benzyl alcohol to toluene under these conditions.

distinguished between purely "thermal" dissociations, giving rise to uncharged particles of the free-radical type, and polar scissions in which both electrons of the bonding pair remain with one fragment. Although the reactions we have been discussing take place under the influence of heat, it is evident from what we have already written that we do not consider them to be of the pure "thermal" type in this sense.

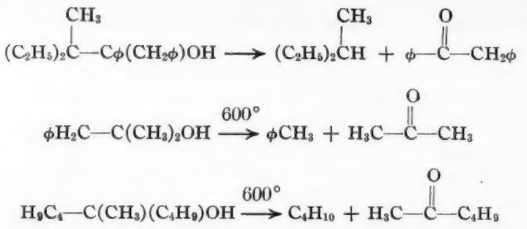
We believe, however, that the dehydrogenation of methanol and other alcohols may properly be so regarded, even though such reactions are subject to heterogeneous catalytic influences (metallic copper being notably effective in this respect). In the purely thermal type of reaction we would be inclined to postulate the initial dissociation of a hydrogen atom from the least electronegative carbon atom of the molecule (the carbinol carbon atom), followed by elimination of the hydroxyl hydrogen atom from the resultant unstable free radical and readjustment to the stable aldehyde or ketone. On the surface of a copper catalyst the reaction mechanism is undoubtedly different in detail, and is probably fundamentally different, although the net result is the same. Obviously tertiary alcohols are structurally debarred from undergoing this type of decomposition. Hence the generalization of Sabatier and Senderens (*41*), confirmed by Neave (*42*), that when alcoholic vapors are passed over a reduced copper catalyst at about 300°, primary alcohols yield aldehydes, secondary alcohols yield ketones, whereas tertiary alcohols are dissociated into ethylenic hydrocarbons and water. (For tertiary alcohols the reaction is essentially uncatalyzed.)

If our view is correct, dehydrogenation will take place at sufficiently high temperatures independently of the presence of any catalyst. As a matter of fact, it is well known that pyrolysis of ethyl alcohol, for instance, often yields both dehydrogenation and dehydration products simultaneously (*43*). It scarcely seems necessary to assume, as Boomer and Morris (*44*) have done, that a given catalyst acts as a dehydrating catalyst at 350°C. and (at least in part) as a dehydrogenating catalyst at 500°C.

It should not be overlooked that the weakest bond (thermally)* in an alcohol is not necessarily a C—H bond. When an alcohol contains a C—C bond which is weaker than, or of about the same order of strength as, its weakest C—H bond, high-temperature dissociation takes place (at least in part) at that point. For example, we cite some data collected by Hurd (*45*).



* By thermally weak bonds we mean those approaching the conformation of type 3 as schematized in Figure 1.



"In general, as temperature . . . increases, dehydration decreases and ketonic scission comes into play. At 650–700° the latter reaction is almost total (except for charring)." Even β-phenylethanol at about 400°C. and constant volume yields some methanol and toluene (*31*), indicating C—C scission as well as dehydration and dehydrogenation.

HEATS OF COMBUSTION

A consideration of heats of combustion is of interest, not only because it throws a physical sidelight on the chemical theories here set forth, but because it illustrates the pitfalls encountered in attempting to make correlations mechanically without due consideration of complicating factors.

If we regard the alcohols as partially oxidized organic radicals we must conclude that a higher state of oxidation has been reached in the alcohols (ROH) containing weakly electronegative radicals (R) than in those containing strongly electronegative radicals. This is merely another way of stating the hypothesis set forth in Figure 2, namely, that the electron-pair constituting the R-to-OH bond is displaced farther toward the hydroxyl group when the radical R is weakly electronegative than when it is strongly electronegative. From this conclusion it is a natural step to the prediction that, upon complete combustion to carbon dioxide and water, the alcohols representing relatively lower states of oxidation should yield relatively greater quantities of heat.

This prediction is in fair agreement with the available data relating to primary, secondary, and tertiary aliphatic alcohols. Some years ago one of us and Sher (*46*) evolved a number of empirical formulas for the calculation of heats of combustion of organic compounds in the liquid state. A more extensive set of formulas, together with a comprehensive compilation of heats of combustion, was subsequently published by one of us (*47*). The formula employed for calculation of the heat of combustion of a primary alcohol is:

$$Q = 26.05N + 13,$$

where N equals the number of electrons exclusive of those associated with the hydroxyl group. For secondary alcohols,

$$Q = 26.05N + 6.5,$$

and for tertiary alcohols,

$$Q = 26.05N + 3.5.$$

The numerical values thus calculated are expressed in kg. cal.$_{15}$ per mole.

It should be noted that all these formulas apply to the *liquid* state,* a fact which has sometimes been overlooked (*48*). Furthermore, the values thus calculated are average values for the classes to which they apply. At the time these formulas were published, sufficiently accurate data to justify attempted distinctions between individual members of a class did not exist. This is still true concerning the greater part of the range of compounds covered.

Rossini (*49*) has recently published a set of "best values" for the first ten normal primary aliphatic alcohols. In Table 2 these values are compared with the average values calculated by means of the first of the foregoing formulas. As should be the case, the calculated value for methanol is considerably too low; that for ethanol is also too low but the discrepancy is less. For the succeeding members of the series, in which the aliphatic radicals differ but little from each other in electronegativity, the calculated and experimental values agree within the limits of experimental error.

TABLE 2

HEATS OF COMBUSTION OF NORMAL PRIMARY ALCOHOLS

$$C_nH_{2n+1}OH\ (\text{liquid}) + \frac{3n}{2}O_2\ (\text{gas}) \rightarrow nCO_2\ (\text{gas}) + (n+1)\,H_2O\ (\text{liquid})$$

Alcohol	*Experimental*	*Calculated*	*Deviation*
Methanol	173.64 ± 0.05	169.3	4.34 ± 0.05
Ethanol	326.66 ± 0.10	325.6	1.06 ± 0.10
Propanol	482.15 ± 0.24	481.9	0.25 ± 0.24
Butanol	638.10 ± 0.32	638.2	
Pentanol	794.30 ± 0.40	794.5	
Hexanol	950.55 ± 0.48	950.8	
Heptanol	1107.05 ± 0.56	1107.1	
Octanol	1263.60 ± 0.64	1263.4	
Nonanol	1420.20 ± 0.72	1419.7	
Decanol	1576.90 ± 0.80	1576.9	

The agreement between experimental and calculated values is admittedly empirical and it is better than should be expected from so simple a formula. It is in part due to the fact that in the liquid state the lower members of the series are associated to a considerably greater degree than the higher members (*50*, *69*). This tends to counteract the error in the assumption that in aliphatic compounds C—C and C—H bonds are thermally equivalent.

So far, for the sake of simplicity in the discussion of thermal data, we have proceeded on the implicit assumption that the electronic influence of the hydroxyl group is completely localized in the R-to-OH bond—an assumption which is inconsistent with the ideas set forth in the earlier articles of this series. Our addendum (13.0 kg. cal.), therefore, is not a simple term representing the average difference between the states of oxidation of carbon and hydrogen in $-\overset{|}{\underset{|}{C}}OH$ and in $CO_2 + H_2O$. It is a composite of that value and of the average effect produced by hydroxyl-induced electronic shifts throughout the alcohol molecule.

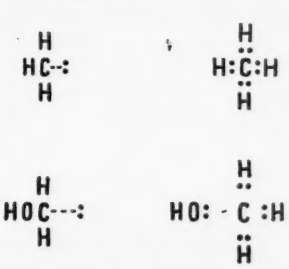
That the composite nature of this term is not to be ignored is brought home to us when we encounter the formula for calculating the heats of combustion of the phenols. Since the phenyl group is more electronegative than the methyl group, phenol must represent a lower state of oxidation than methyl alcohol. Consequently, in view of the oversimplified treatment just outlined it would appear anomalous that the basic empirical formula† for phenols is identical with that for tertiary alcohols, with a correction factor of 3.5 kg. cal. rather than one greater than 13.0 kg. cal.

$$Q = 26.05N + 3.5$$

This startling denouement, however, is readily attributable to its true cause, and, in fact, constitutes only the realization of a probability which was predictable from the first. Let us now retrace our steps with due consideration for electron shifts induced throughout the alcohol molecule by the hydroxyl group.

The elementary theory of heats of combustion has been discussed in some detail in the first two articles of this series (*1a*, *b*) and elsewhere (*47*); hence repetition here is undesirable. It should be fairly obvious, however, that if electrons are in general shifted outward from carbon nuclei by the introduction of the hydroxyl group into a hydrocarbon molecule, the heat of combustion of the resulting hydroxyl compound should be greater than it would be if the electrons remained undisturbed. This effect is the one which our theory would require for the aliphatic alcohols in general.

From the ideas set forth in the earlier articles of this series it necessarily follows that the hydroxymethyl radical should be less electronegative than the methyl radical. The difference in the electronegativities of these radicals should be reflected in the respective electronic configurations of their corresponding hydrides, methanol and methane.



With suitable elaborations the same argument may be applied to all the saturated aliphatic alcohols. We thus see that for the aliphatic alcohols the addendum

* On theoretical grounds it would be preferable to employ values for the gaseous state and thus eliminate (or at least minimize) complications due to intermolecular forces. Unfortunately, sufficiently accurate data are available for relatively few compounds. For non-polar compounds the error introduced in this way is smaller than the experimental error in most cases. For polar compounds the errors introduced are, to a considerable extent at least, self-compensating.

† Correction terms are added for aliphatic-to-aromatic bonds in substituted phenols. *Cf.* KHARASCH (*47*).

in our empirical formula may be expressed by the sum of two positive terms, say $+ p + q$. The first represents the additional heat which will be liberated in passing from the state of partial oxidation, —COH, to the state of complete oxidation, $CO_2 + H_2O$. The second represents the heat increment inherent in the difference between the electronic configurations of the methyl radical in methane and in methanol. It is probable that the second term, q, remains practically constant throughout the series of normal primary alcohols above butanol, although there are doubtless slight deviations in the first members of the series. We have already indicated in connection with Table 2 that $p + q$ is, as our hypothesis requires, larger than 13.0 kg. cal. for methanol and ethanol.

Turning to the phenols, we see immediately that a different situation confronts us. There are numerous and excellent chemical reasons for supposing that the hydroxyphenyl radicals (like the anisyl radicals) are all more electronegative than the phenyl radical. If for convenience we compare the hydride of an imaginary composite average of the three possible hydroxyphenyl radicals (phenol) with the hydride of the phenyl radical (benzene) it appears that the relationship between their respective electronic configurations is the reverse of that which we discovered in the methanol-methane comparison. The addendum in our empirical formula has again been split into two terms, but now one is positive and the other is negative, say $+ p' - q'$. We need not, therefore, be greatly taken aback to find that on the average,

$$+p + q = 13.0 \text{ (for primary alcohols above butanol)},$$

whereas:

$$+p' - q' = 3.5 \text{ (for phenols)}.$$

REACTION WITH METALS

So far we have concerned ourselves chiefly with those properties of alcohols which vary in accordance with the nature of the C—OH bond. Let us now turn our attention to the O—H bond.

It is an established generalization that the hydroxides of the strongly electronegative elements, like chlorine, are acidic, that the hydroxides of the very weakly electronegative elements, like sodium, are basic (in the old-fashioned sense that they tend to liberate hydroxyl ions), and that the hydroxides of elements intermediate in the scale of electronegativity are either amphoteric or non-electrolytic. The implication is that the polarity of the O-to-H bond in the hydroxyl radical increases in direct ratio to the electronegativity of the group attached to the hydroxyl group. It is, therefore, a question of considerable interest whether or not an analogous gradation of bond polarities may be discovered in a series of organic hydroxides covering a wide range of radical electronegativities. The effect which might naturally be sought is *qualitatively* schematized in Figure 3.

There can be no doubt that one extreme of the table is consistent with the scheme proposed, for the naphthols and phenols are definitely acidic. Even methanol and ethanol, though extremely weak acids indeed, are measurably acidic.* The other extreme of the table does not furnish evidence quite so conclusive, for the triarylcarbinols apparently are not electrolytes except in such a strongly associative solvent as SO_2, where even trimethyl carbinol exhibits some conductivity (*52*). Nevertheless, as we have already noted, the hydroxyl can be removed from these alcohols with remarkable ease. Indeed, mention of their "basic" properties is a commonplace in the literature, and the products of their reactions with the mineral acids be-

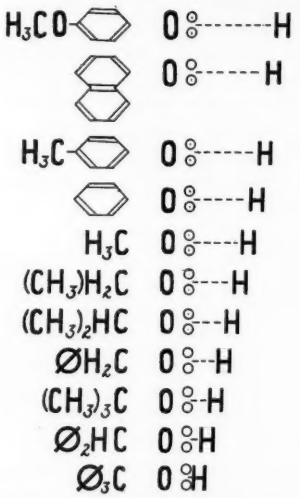


FIGURE 3.—QUALITATIVE REPRESENTATION OF SOME TYPICAL RO-TO-H BONDS

have in many cases like true salts. In order to put the intermediate members of our series to the test, however, we shall have to turn to some non-ionic reaction. We have a convenient test of this kind in metallic reduction.

There has been considerable confusion of thought on the subject of the displacement of hydrogen from compounds by metals. Some organic chemists have been prone to assume that such a reduction is a definite criterion of "acidity," even when the "acid" in question does not yield protons to so protophilic a solvent as liquid ammonia. Some inorganic chemists, on the other hand, have assumed that ionization is a necessary prelude to the liberation of hydrogen from an acid by a metal.

* We should perhaps add at this point that we do not believe that after the definitely acid range of compounds has been reached a direct correlation can be made between radical electronegativity and acid dissociation constant [*cf.* the preceding article of this series (*1c*, p. 85)]. Incidentally, the apparent anomaly represented by the carboxylic acids (which would not be expected to display acidic properties at all on the basis of the ideas here outlined) is attributable to the fact that their structures are not truly represented by the formula $RC\langle^{O}_{OH}$. [*Cf.* LEWIS (*51*).]

We have pointed out what we believe to be the fallacy of the first of these notions in the second article of this series (*1b*, pp. 1740–2). Kilpatrick (*53*, *54*) has demonstrated that the other is erroneous.

It follows from the hypotheses developed in these articles that there must be two types of compounds from which hydrogen is liberated by the more active metals: (1) those in which hydrogen is attached to a strongly electronegative group and is therefore sometimes said to be "positive"; and (2) those in which hydrogen is attached to a very weakly electronegative group. The first type includes the true Brönsted-Lowry acids, H_3O^+ among them, and what we may term the "near-acids"—compounds which do not yield protons even to very protophilic solvents, but which nevertheless contain polar hydrogen covalences in which the electrons are markedly displaced away from the hydrogen atom. Many of the alcohols and acetylene fall in the latter sub-class. The second type we shall not discuss further here, except to cite triphenylmethane and germane as typical examples. The great intermediate class of compounds in which hydrogen is joined to groups neither very strongly nor very weakly electronegative is inactive toward metals. (Compare the classification of R-to-carboxyl bonds in the preceding article of this series.) In each of the groups which lie outside the intermediate range reactivity toward metals increases as one proceeds away from the mean and toward the extreme.

A rapid survey of the experimental facts confirms the trend of reactivity which might be predicted from a consideration of Figure 3. Hemilian (*13*) reported that triphenylcarbinol is indifferent to sodium amalgam. Schlenk and Mair (*55*) obtained no reaction by heating a xylene solution of the carbinol in the presence of metallic sodium, but did succeed in obtaining the sodium derivative by adding particles of the metal to a molten bath of the carbinol maintained at 185°C. under an atmosphere of nitrogen.

Bacon (*56*) prepared the sodium derivative of benzhydrol by dissolving the carbinol in five volumes of absolute ether and refluxing in the presence of the calculated amount of sodium wire until the metal had disappeared. The time required is not stated.

Tertiary butyl alcohol is sufficiently resistant to metals to permit the drying of it over sodium at room temperature (*57*). The sodium derivative can, however, be prepared in rather poor yields by refluxing an excess of the carbinol in the presence of the metal and subsequently distilling off the excess carbinol (*58*, *59*). Bischoff reports that, when the carbinol was dissolved in ligroin and heated over metallic sodium for 20 hours, some traces of the metal still remained (*59*). Menschutkin (*60*) reports that trimethylcarbinol forms no alcoholate with baryta and adds that this is a general characteristic of the tertiary aliphatic alcohols, distinguishing them from the primary and secondary.

When Lowe (*61*) treated benzyl alcohol with metallic sodium he found the reaction so sluggish that he resorted to warming to expedite it.

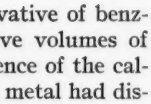
The sodium derivatives of isopropyl and secondary butyl alcohols are prepared by adding less than the calculated quantity of metal and distilling off the excess alcohol (*59*, *62*).

Ethyl and methyl alcohols both react readily with sodium at room temperature. Absolute methyl alcohol, heated with clean magnesium in a sealed tube for three hours at 200°, gives a quantitative yield of pure hydrogen. The residue gives the correct analysis for $(CH_3O)_2Mg$. Clean magnesium also reacts slowly with absolute methanol at room temperature (*63*). According to Meyer and Jacobson (*64*) ethyl alcohol does not react with magnesium at room temperature but does upon heating.

The phenols and naphthols, as we have already remarked, are definitely acidic and behave toward metals in general like weak acids. When treated with metallic sodium in organic solvents they undoubtedly yield their metallic derivatives chiefly through molecular reduction rather than through the discharge of hydrogen ions.

ESTERIFICATION

At least some mention of esterification is properly to be expected in any general discussion of the chemistry of compounds of the alcohol type. Unfortunately, anything like a comprehensive discussion of this reaction would require a separate paper in itself. At the present time, therefore, the writers must content themselves with presentation of the barest outline of their views in the hope that this may suffice, together with the general principles so far expounded in this series, to suggest profitable lines of thought and experimentation to the reader.

It is well to approach consideration of this reaction in the full realization that the problems it presents are not so simple, from either the theoretical or the experimental standpoint, as they might appear superficially. To begin with, we have in the esterifying acid a compound which is not adequately represented by the ordinary structural formula  . If we are content to ignore such minor complications as association it is probable that in fairly concentrated solution and/or in the presence of strong mineral acids the average carboxylic acid (of which we may consider acetic acid to be representative) is a tautomer approximately depicted by such a formula. In short, it is only in an environment in which a carboxylic acid is least an acid that the ordinary structural formula approaches validity at all. This must be kept in mind in any theoretical speculations involving detailed concrete representations of mechanism.

The acid component of the system further complicates the esterification reaction by reason of its tendency to play the dual rôle of reactant and catalyst. It necessarily follows that the reactivities of two carboxylic acids cannot be estimated merely by treating fixed molar quantities of the respective acids with a

fixed molar quantity of a given alcohol; the two reactions will then be catalyzed to different degrees. Conversely the reactions of a given acid with two different alcohols are not strictly comparable, for the acid will be a better catalyst in one alcohol than in the other. This complication is probably not significant when closely related alcohols (say methyl and ethyl) are compared, but it increases as the difference between the alcohols becomes greater. Ingold (*65*) has emphasized the importance of pH as a factor to be considered in arranging comparable experimental conditions for the study of rates of proton- and/or hydroxyl-catalyzed reactions and has suggested that the pH of minimum rate (designated as pH*) be adopted for the comparison of ester hydrolyses. This factor does not, however, seem to have received the attention it deserves in esterification-rate studies.

Still another complication arises in the probable duality of the esterification mechanism. Apparently it is now generally recognized that the resemblance of the reaction of an alcohol with a carboxylic acid to that of an alkali hydroxide with a mineral acid is purely formal and stoichiometric, and that from the standpoint of reaction-mechanism it is the *distinction* between the two phenomena that should be stressed. Williams and Truesdail (*66*) have outlined what is probably the commonly accepted view of esterification at the present time. They regard the reaction as a special case of mixed anhydride formation and postulate that the molecule of water eliminated is composed of a hydrogen atom (or ion) derived from the alcoholic hydroxyl group and an hydroxyl radical (or ion) derived from the acidic carboxyl group.

In so far as this mechanism applies to esterifications like that of ethyl alcohol with acetic acid the present writers believe it to be essentially valid. However, it seems probable that only a portion of the entire picture is here presented. Prévost (*67*) has suggested the possibility of two distinct alcohol-acid esterification mechanisms and has expressed the belief that the esterification of, say, ethyl alcohol with a strong organic acid (*e. g.*, trichloracetic) is analogous to halide formation, which we have already discussed in some detail. We would like to amplify Prévost's suggestion somewhat by pointing out that the nature of the individual alcohol undergoing esterification should be taken into consideration along with the strength of the esterifying acid.

Prévost's hypothesis might be summarized by specifying that when RCOOH represents a weak acid and R′COOH a strong acid the following mechanisms may be assumed for a given alcohol:

$$RCO|OH + H|OR'' \rightleftharpoons RCOOR'' + H_2O \qquad (1)$$

$$R'COO|H + HO|R'' \rightleftharpoons R'COOR'' + H_2O \qquad (2)$$

Incidentally, the formal resemblances between the mechanisms thus suggested and those of two other well-known reactions for ester preparation are striking.

$$RCO|X + Na|OR'' \rightleftharpoons RCOOR'' + NaX$$

$$R'COO|Na + X|R'' \rightleftharpoons R'COOR'' + NaX$$

We suggest the supplement to Prévost's hypothesis that when ROH represents an alcohol containing a strongly electronegative radical (R), R′OH an alcohol containing a weakly electronegative radical (R′), and R″COOH a given acid of moderate strength:

$$RO|H + HO|OCR'' \rightleftharpoons ROOCR'' + H_2O$$

$$R'|OH + H|OOCR'' \rightleftharpoons R'OOCR'' + H_2O$$

With two variables to be taken into consideration it is evident that the duality of mechanism suggested may extend over a considerable range of reactants and may tend toward confusion in the conclusions to be drawn from comparative reaction-rate studies. Indeed it is not at all inconceivable that under the usual laboratory conditions both mechanisms may operate simultaneously in the cases of certain acid-alcohol combinations.

Finally, we must not forget that instability of reaction product often goes hand in hand with ease of reaction, and that the ever-recurrent question of reactant and product solubilities cannot be ignored.

It is therefore obvious that quantitative comparisons between various sets of data recorded in the literature are utterly impossible, and even that it would be very difficult to discover a single set of quantitatively self-consistent data. We shall content ourselves with brief comment on the famous studies of Menschutkin (*8*, *60*, *68*) which led to the generalization cited earlier in this paper.

Menschutkin's comparative reaction rates for the esterification of alcohols with acetic acid (and acetic anhydride) have been tabulated in so many textbooks, reference works, and theoretical articles that there is little justification for copying them here. It is probable that in the esterification of aliphatic primary and secondary alcohols with acetic acid the first of the reaction mechanisms suggested by Prévost predominates, and to this extent the recorded data are qualitatively (though not quantitatively) comparable. On the basis of the ideas set forth by the present writers it might be expected that, in a reaction mechanism of this kind, a series of alcohols would display approximately the same relative order of reactivity as they do toward metals. Plainly this is the general trend.

As regards the tertiary alcohols, it is probable that the second of the mechanisms proposed by Prévost comes into play to a significant extent. Such a mecha-

nism would involve the temporary liberation of positive tertiary aliphatic ions (or of some corresponding complexes) which, under the conditions of the experiment, would be expected to lead to considerable olefin formation. That is precisely what occurs. The small amounts of tertiary esters obtained under these conditions probably arise in part from mechanism (1) and in part from mechanism (2). Therefore, the writers do not believe that the data for tertiary alcohols are even qualitatively comparable with those for primary and secondary alcohols. The apparent agreement of these data with the trend which might be expected upon the basis of an uncritical application of the writers' ideas is regarded as largely fortuitous.

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DEVELOPING *a* PROFESSIONAL ATTITUDE *in the* UNDERGRADUATE CHEMISTRY STUDENT*

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MUCH has been written upon the value of a liberal arts course in the early training for the professions of medicine, engineering, and the natural sciences. Educators in the leading professional schools in these fields have shown in recent years a pronounced disposition to select for advanced work students who have received a broad cultural background in their undergraduate training. So much emphasis has been placed upon liberalizing the college curriculum that the instructor of undergraduate science courses may well question to what extent he can consider his teaching as contributing to the progress of his science. With few exceptions, however, the instructors are themselves professionally minded, and in many institutions they have a class consciousness which at times proves annoying to their colleagues teaching less professionalized subjects. Unless the instructor imbued with such a spirit can find ways to pass on to his major students the enthusiasm he feels for his profession, he will not only continue to prove a disgruntled member of the college family, but his students will miss a point of view that can mean much to them in the present and the future. The following suggestions on the development of a professional attitude in the undergraduate student are some which have served as a safety valve for the author's own professional ambitions, and they thus far have brought forth no restrictive actions by his less technically minded colleagues.

The first step in the development of a professional consciousness in the student is the separation of all science majors from those who are enrolled in the first-year chemistry course just because it is a subject required for graduation. While there is little agreement among educators on what should be given the pandemic group, the segregation of the students who expect to make use of the science in a professional way gives an opportunity for the training of the latter group in a theoretical and technical manner that could never be realized in a mixed class. Chemistry demands a mathematical presentation from the first, and modern laboratory manuals are requiring a manipulative skill beyond what could be expected of the student who does not plan to go beyond the first year. After ten years' experience in grouping the science majors into separate sections of elementary inorganic chemistry the author is convinced that this one step has done more to raise the scholastic standards of the department than any plan which has come under his practice or observation.

Professional methods and points of view may be continued from the first-year course into all the branches of chemistry taught in the department. Quantitative analysis presents an excellent opportunity to stress the importance of never submitting a report on an analysis until the student is ready to stake his reputation on its accuracy. Insistence upon this professional point of view will lessen the student's natural inclination to work just for a grade, or to be satisfied with merely getting by the analysis without having to repeat it.

The course in elementary organic chemistry often degenerates into memorizing the methods of preparation and the properties of one class of compounds after another unless some means is found of vitalizing the process, and of getting the student to visualize some of the future applications he may make of his knowledge. A practical test that will challenge the student's command of methods of preparation may be developed by requesting him to synthesize a series of compounds from a given set of starting materials. This exercise is much more stimulating than the cataloging of methods of preparation, and as the student's skill in organic syntheses increases, more exacting discussions of the specific experimental conditions for each step in the preparations may be required. The necessary drill on the properties of the more common classes of compounds may be given a practical turn by demanding that the student separate a given mixture of such compounds, or that he set about to establish the structural formula of an unknown organic compound. A final means of making the training in elementary organic chemistry less academic is to turn to the field of commercial organic syntheses, and there point out example after example of large-scale production by methods which are not even listed as possible in the student's textbook.

The undergraduate course in physical chemistry offers the best opportunity of all to appeal to the professional spirit, for it is here that chemistry may be portrayed as a science undergoing rapid changes of the

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most fundamental nature. Developments in the fields of atomic and molecular structure, the theory of solutions, catalysis, colloids, photochemistry, and thermodynamics cannot fail to arouse in the student an intense interest in the almost day-by-day advance in each, and from this vantage point it is only a step for the superior student to want to qualify to take his place in the onward march.

Mention of the superior student brings to our attention the exceptional advantages for professional advancement which have been made possible through the so-called honors course as developed in a number of institutions. The student who can qualify for this is in a position to enter two phases of professional training which normally are achieved only by the graduate student, namely, the honors thesis and the comprehensive examination. An early introduction to elementary problems of research gives the student an excellent opportunity to cultivate habits of independent thinking, while the comprehensive examination requires that he master on his own initiative a working knowledge of a broad field. Superior students can arise to the challenge of these situations to a remarkable degree, but to place the same privileges before the average undergraduate is to invite superficiality and a loss of perspective. The author has known a superior student to obtain a mastery of the calculus through private study that was superior to that which could be demonstrated by a class after a year of instruction; on the other hand, he has seen a number of average students on a comprehensive examination fail to write a critical discussion of a single topic of theoretical chemistry at the close of four years' work in the department.

The development of a professional point of view in the undergraduate chemistry student depends more upon the attitude and standing of his instructor in the profession than upon the method or content of the courses he takes. As stated in the introduction, if the instructor is content to yield to the pressure from the professional schools and from his own college administration to teach his science merely as a cultural subject, there is no need for him to concern himself over his standing in the chemical profession. If, however, he believes he can make a worth-while and timely contribution to the professional life of the student through his own example then he may find the following suggestions borne out in his own experience.

An active personal interest in research will prove the greatest single challenge an instructor can give his students. It is most difficult, unfortunately, for the teacher of undergraduates to keep alive his own ambitions in the realm of productive scholarship. He is expected to pass so many of the mentally indolent and poorly prepared members of his elementary classes that for the conscientious instructor with even average standards of scholarship, this calls for many extra hours of individual coaching, cajoling, and threatening. In the smaller institutions there must be added to this the handicaps of limited library and laboratory facilities, and the increased demand placed upon the members of the college faculties to assume positions of leadership in the varied phases of community life. And in recent years both college and university men have been compelled to seek outside sources of income to supplement salaries which in some instances were reduced below that which provided the necessities of life.

In spite of these unfavorable circumstances the instructor who appreciates the value to himself and his students of his active pursuit of research will find ways and means for this activity also. His contributions will not approach in scope or brilliance those which are carried out by workers devoting their full energies to research, but the growing volume of literature from the smaller institutions is evidence that the results are counted worthy of recognition by the editorial boards of the Society's journals. The mental discipline required to bring the work to full fruition, rather than any recognition accorded the same, constitutes its most lasting reward, and only the instructor who has labored under these conditions can evaluate the stimulating effect it exerts on all phases of his teaching.

Active membership in scientific societies is another means of professional development so patent that few can afford to neglect it. The American Chemical Society in particular, through the meetings of the local sections and the semiannual gatherings of the whole Society, opens up a number of avenues for professional advancement. While most of the programs of both the local and national meetings are devoted quite properly to recent advances in theoretical and applied chemistry, the instructor of undergraduates will receive more profit from these sessions, and from contacts with the men who achieved these discoveries, than he could derive from meetings of just the Division of Chemical Education alone. Happily, the leaders of this Division still retain the emphasis upon chemistry rather than education in every session of this group, and as long as chemistry continues to advance at its present rate, most of us will seek every opportunity to remain abreast of the best thought of the science, although our methods of teaching and philosophy of education may trail those of other more stabilized fields. Even those of us who are loaded down with teaching and administrative duties like to think of ourselves first of all as chemists.

For the final suggestion on professional development we turn to what some consider a duty, and others a privilege, of the teacher, that of following our students after graduation. We miss one of the richest experiences of all if we fail to maintain a personal interest in our graduates, particularly during the early years of their professional careers. For those who enter industry direct from their undergraduate studies, there are many adjustments to be made, and promotion is discouragingly slow. Those who are fortunate enough to enter immediately upon graduate work will find the transition less abrupt, and there will be one or more years in which they can judge progress by familiar landmarks. Personal contacts with both groups, however, will result in increased effort on the part of the students, and to the instructor they will bring a sense of

achievement not to be found in any other phase of his work, for if we did not believe in our ability to count for more through the training of others than through the exercise of our own talents in pure and applied science, we must admit ourselves as misfits in the scheme of things.

On the other hand, the instructor who can find in the work of his former students that which he himself could not accomplish has achieved a state of mind which will enable him to develop in his undergraduates a professional consciousness that will challenge them to higher levels. A professional attitude that can be deeply rooted in the undergraduate chemistry student is seed that will bring forth fruit in due season.

INTRODUCTION *to* ISOMERISM *and* STRUCTURAL THEORY

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STUDENTS usually become acquainted with structural theory—the basic principle of modern organic chemistry—at the beginning of their study of organic compounds. It is of utmost importance that the empirical foundation of this theory should be clear to them from the very start. Structural theory should not appear to the students as the expression of a scientific fantasy, but as a reflection of the essence of things. It is also of importance that students should understand how, starting from the chemical properties of substances, we come to explain the structure of their molecules and, on the other hand, how we can judge the chemical properties of substances on the basis of their formulas. In other words the student should understand that structural formulas are not only a formal expression of the interlinking of atoms, but—and this is of particular importance—that they reflect the chemical "behavior" of the substance, that is, they represent formulas of "reaction."

Finally, it is of importance to select experiments which students can easily grasp, and which are comparatively easy to demonstrate in classroom work or in practical laboratory work.

Lothar Meyer stressed in his time the pedagogic importance of a non-dogmatic approach to structural theory. "Research on the 'structure' of compounds represents one of the principal tasks of scientific chemistry, particularly 'organic' chemistry, which deals with carbon compounds. Owing to the untiring efforts of many scientists, this research work has resulted during the last fifty years in so complete and definite a knowledge, that this knowledge began to appear in textbooks in quite a dogmatic way, as an accepted truth, without exact explanations as to the road which leads to the deeper understanding of the subject. It would, however, be desirable that every person who intends to take this matter up thoroughly should be well acquainted with the facts upon which our knowledge is based. Besides, for the general history of culture and, in particular, for the history of science this vast research work is a remarkable instance of the penetration of the human mind into a subject inaccessible to direct sensual perception." (L. Meyer, "Foundations of theoretical chemistry.")

Our personal experience leads us to believe that we have succeeded in selecting subject matter which satisfies the above-mentioned requirements.

ETHYL ALCOHOL AND METHYL ETHER AS EXAMPLES OF ISOMERIC SUBSTANCES

Students should first be shown the necessity of considering molecular structure and of introducing structural formulas; it should become clear to them why the method of representing the composition of a substance, usually accepted in inorganic chemistry, proves to be insufficient as soon as we come to deal with organic compounds.

Isomeric phenomena offer a natural introduction to the conception of molecular structure. It naturally follows that acquaintance with these phenomena should precede acquaintance with the basic principles of the structural theory.

We could find, of course, a wide variety of examples suitable for a first study of isomeric phenomena. The majority of textbooks mention butane and isobutane as first examples of isomeric substances. We consider these substances as the least suitable. It must appear entirely incomprehensible to the student, why we attribute a structure with a normal chain of carbon atoms to a substance with an empirical formula C_4H_{10}, boiling at 1°, while to a substance with the same empirical formula, boiling at 17°, we attribute a structure with a ramified chain. It is clear that in the first stages of instruction we cannot as yet refer the students to reactions which could be made use of for the explanation of the structural formulas of butane and isobutane. We are, therefore, compelled to proceed dogmatically.

Ethyl alcohol and methyl ether are much more suitable objects. These substances differ sharply from each other, the difference in their chemical properties being of such nature that it can be made use of for the representation of their structural formulas in the beginning of the course. The students know ethyl

alcohol from everyday experience. Methyl ether, as we shall state somewhat later, can be easily obtained in laboratories. Therefore, we have selected these substances as the first examples with which to illustrate isomeric phenomena and the methods of establishing molecular structure.

To begin with let us take ethyl alcohol. Students become experimentally acquainted with its physical properties (its solubility in water, its specific gravity, its boiling point); they make by the most simple method a qualitative (and, if possible, a quantitative) analysis, thus becoming acquainted with the methods of analysis of organic substances. From the results of the analysis (either obtained experimentally, or imparted by the teacher) a simple formula for ethyl alcohol is deduced. (We do not describe this work, as the method is sufficiently known.) The data obtained from this experiment serve the students for the computation of the molecular weight of alcohol. Thereafter the teacher demonstrates the experiment showing the way to determine the density of alcohol vapor according to the Gay-Lussac-Hoffman method. Thus students become convinced that the simplest formula of ethyl alcohol represents at the same time its molecular formula.

The next step in our work is to show that the properties of methyl ether differ from those of ethyl alcohol, though both have the same molecular formula.

Methyl ether is not produced commercially and we have met no indication in the literature that this substance is used for experiments in the course of chemical instruction.

We had, therefore, to work out methods for all experiments pertaining to this work. As a source of methyl ether we suggest the use of its solution in sulfuric acid. The solution is prepared in advance of the lecture according to the method of Erlenmeyer. A mixture of 1.3 parts (by weight) of methyl alcohol with 2 parts of sulfuric acid is placed in a flask with a reflux condenser and gradually heated to 140° (the thermometer immersed in the liquid). Ether begins to form at 110°, and at 140° the process is completed. The gas is passed through a solution of lime and is caught in a glass jar filled with concentrated sulfuric acid, which is cooled by a cold water bath. At normal temperature one volume of acid dissolves about 600 volumes of ether. When this solution is added drop by drop to water, the ether is liberated almost completely, as it is practically insoluble in water.

The following experiments can be carried out by students with this solution. Three to four drops of the solution are added to two to three cubic centimeters of water in a test-tube while the students watch the evolution of gas and note its odor. A few drops more of the solution are added and the discharged gas is lighted. Thus one can see the flame produced by the ether.

If desired, a kind of "ether burner," shown in Figure 1, can be demonstrated. *A* is a test-tube filled with water; *B*, a pipet, is filled with the solution. The screw clamp, *C*, is regulated in such a way that the solution passes into the test-tube drop by drop, and after the air has been displaced, the gas issuing from the outlet tube is lighted. In order to obtain a steady discharge of gas, it is best to place a small piece of pumice stone or of an unglazed earthenware plate in the test-tube. The test-tube can, of course, be replaced by a small flask, and the pipet by a dropping funnel. The students can thus satisfy themselves as to the fact that the properties of methyl ether actually differ distinctly from those of ethyl alcohol. Data on the quantitative composition of methyl ether are supplied by the teacher; the students see that the simplest formula of ether coincides with that of ethyl alcohol. The next step is to prove that the molecular formulas are also identical. This proof is more impressive if the students themselves make the respective determinations.

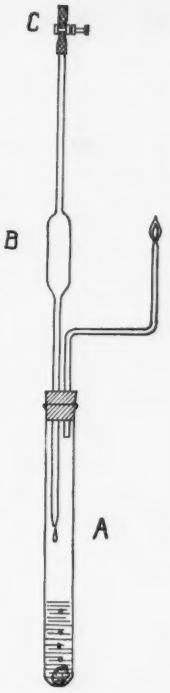


FIGURE 1

We have worked out a method of determining the density of methyl ether so simple that it can be included in the student's independent experimental work. We devised the apparatus shown in Figure 2. *A* is a flask with a dropping funnel which serves as a generator for methyl ether; *B* is a Woulfe bottle filled with water. At first, the apparatus to obtain methyl ether is disconnected from the Woulfe bottle; the screw clamp, *C*, is closed; about 5 to 10 cc. of water is poured into the flask, and a piece of pumice stone is placed therein, while 2 to 5 cc. of methyl ether solution in concentrated sulfuric acid is poured into the funnel. The apparatus thus prepared is placed on scales (it suffices to determine the weight with an accuracy of 0.01 g.). After having sucked water into the siphon we close the pinch clamp, *d*, and lower the end of the siphon into a beaker. The apparatus, *A*, is

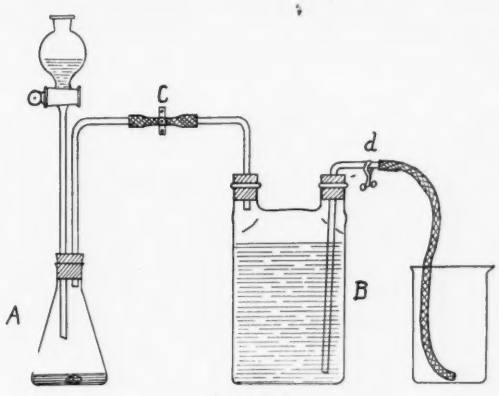


FIGURE 2

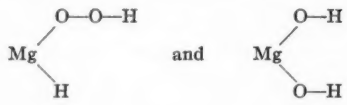
then connected with the Woulfe bottle, the clamps, *d* and then *C*, are opened and the solution is added drop by drop to the water;* the gas formed forces the water out of the bottle. When the evolution of gas ceases the flask is cooled and the water levels in beaker and bottle are adjusted to bring the gas to barometric pressure. The clamp, *d*, is then closed and the volume of water accumulated in the beaker is measured.

The volume of methyl ether, determined in this way, is reduced to standard conditions by calculation. The apparatus for obtaining methyl ether is weighed again and the loss in weight is taken as the weight of the discharged gas. It is, of course, very easy to calculate on the basis of the quantities found, the density of methyl ether. If the work is carefully done divergencies from theoretical data never exceed one per cent.

STRUCTURES OF INORGANIC COMPOUNDS

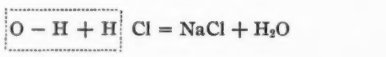
Before we begin to study the molecular structures of ethyl alcohol and methyl ether, it is advisable to recall to students all they have learned during their study of inorganic chemistry about valency and molecular structure in general. It is of greatest importance to show the students by means of simple, familiar examples that the problem of the structures of molecules cannot be solved solely on the basis of the valency of atoms forming the molecules. Let us consider the following two examples.

As the results of analysis show, the formula for the hydrate of magnesia is MgO_2H_2. Upon the basis of this formula, taking into consideration the fact that magnesia and oxygen are bivalent, while hydrogen is univalent, we find that the following combinations of atoms which conform to the given formula are possible:

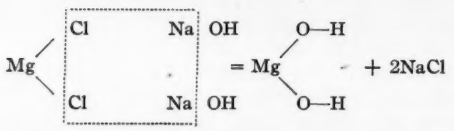


It is easy to prove that only the second of these formulas corresponds to the hydrate of magnesia. Let us, for instance, examine the following reactions:

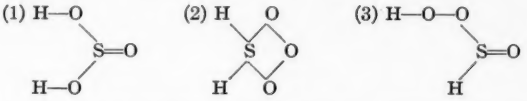
$MgO_2H_2 + 2HCl = MgCl_2 + 2H_2O$. This reaction is identical with that of hydrochloric acid and sodium hydroxide, the structure of which is, Na—O—H

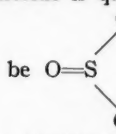


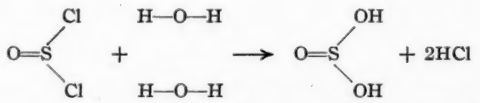
In both cases water and a salt are formed. Since water is formed through the combination of the hydroxyl of the base with the hydrogen of acid, and since two molecules of water are formed in the reaction of hydrate of magnesia with hydrochloric acid, it is evident that the molecule $Mg_1O_2H_2$ must contain two hydroxyl groups. This is confirmed by the following reaction:



A second example: we get by way of analysis the following formula for sulfurous acid: H_2SO_3. For the quadrivalent sulfur, bivalent oxygen, and univalent hydrogen several expressions are conceivable, as for instance:



In order to prove the correctness of the first formula we can refer to the reaction of thionyl chloride with water. Sulfur in thionyl chloride is quadrivalent, so that its structure can only be  . Upon interaction with water thionyl chloride forms sulfurous acid and hydrogen chloride. This reaction can have but one equation:



The analysis of such examples is of great use to students since these formulas prove to them: (1) that there can be cases when an empirical formula would cover not only one definite combination of atoms, but several different combinations; (2) that in the molecule of each given combination atoms are linked in a definite unchangeable order; and (3) that the order in which atoms are linked to each other in the molecule of a given substance can be determined by studying the chemical properties of the substance.

THE STRUCTURAL FORMULAS OF ETHYL ALCOHOL AND METHYL ETHER

Let us now proceed to determine the structural formulas of ethyl alcohol and methyl ether. We could choose the way already used with inorganic substances in the above-mentioned case, that is: we could first construct the structural formulas (for the compound C_2H_6O there can be only two) and then determine according to the chemical properties of ethyl alcohol and methyl ether which formula must be ascribed to each of them.

As regards ethyl alcohol we believe that another method would be more suitable: we mean to study first the chemical properties of the substance and then deduce its structural formula. Though this method may seem somewhat more complicated than the first one, it pays to follow it, as it leads to more valuable results.

* It is clear that only part of the solution can be added.

This second method is, actually, the true road of scientific research. By following it the student obtains an adequate idea of the methods followed to determine the structure of a substance and of the criteria which must be used in this work.

First we must examine the chemical properties of alcohol. This does not mean, of course, that all the known reactions of alcohol have to be considered. To form an idea of its structure it is sufficient to examine the reactions yielding products of *structures already known to the students*. The reaction of alcohol with hydrogen bromide, $C_2H_6O + HBr \longrightarrow C_2H_5Br + H_2O$, can serve for this purpose. (If time permits, the experiment of producing ethyl bromide can be demonstrated; otherwise it might suffice to show a sample of the compound.)

The formation of water in this reaction should be explained. The structural formula of water is already familiar to the student. Therefore, we go on to analogous reactions already known to the students from their study of inorganic chemistry. Water, for instance, is formed in a neutralization process.

In this case water is formed through a combination of acid hydrogen with the hydroxyl of the base. We can surmise that in the case of the above-mentioned reaction water formation is also due to a combination of hydroxyl groups with hydrogen. Since, in order to unite with carbon, the univalent bromine atom must first yield up its hydrogen atom, it is more than probable that the molecules of hydrogen bromide are the source of hydrogen: in that case the molecules of alcohol must be the source of the hydroxyl groups. The alcohol molecule can be regarded as a combination of the hydroxyl group with the group C_2H_5.

This interpretation of the reaction is based upon the assumption that in alcohol the atoms of hydrogen and of oxygen are connected with each other in the same way as in water. But to a person without any previous knowledge (and as such students must be regarded), such an assumption might appear arbitrary: it may be possible that there are no "ready" hydroxyl groups in the alcohol molecule, and that they are formed during the process of the reaction by means of combination of an atom of oxygen with one of the atoms of hydrogen attached to carbon.

Consequently, facts must be brought out which would confirm that hydroxyl represents a structural element of the molecule of alcohol. At this point it would naturally occur to use the synthetic method, taking a substance in which the presence of hydroxyl groups has already been proved.

Unfortunately, the hydrolysis of ethyl bromide is not well adapted to classroom demonstration. It remains, therefore, to inform the students in a special talk on this subject that the reaction of ethyl bromide with water has been often repeated and that it has been finally proved thereby that the products of this reaction are alcohol and hydrogen bromide. It is also advisable to mention in this connection the causes which make it impossible to demonstrate a corresponding experiment during the lesson. These causes are: (1) the necessity of conducting the reaction under pressure, and (2) the time required for the process. The latter factor can be made the occasion for an introduction of the problem of reaction velocities.

The results of this work give sufficient data confirming the existence of a hydroxyl group in the molecule of alcohol. Therefore, the students can change the original formula C_2H_6O into C_2H_5OH. The reactions studied before are once more examined. To see which groups have passed unchanged from one combination into the other we can introduce the conception of ethyl as of an organic radical. Thus the significance of the formula C_2H_5OH changes: it shows that the alcohol molecule can split into two groups of atoms—ethyl and hydroxyl. We shall not now encounter any difficulties in constructing a complete structural formula of ethyl alcohol, the radical C_2H_5 admitting of only one structure.

If we examine the formula just evolved, we shall find food for new conclusions, that is, that the location of one hydrogen atom in the molecule of ethyl alcohol differs from the location of the rest of the hydrogen atoms. This fact must be reflected in some way in the chemical properties of the alcohol. And actually, experiments show that of all the hydrogen atoms only one can be replaced by sodium.

Here again we have found a way to avoid mere references to experiment, introducing instead the experiment itself.

If we gradually add a definite weight of alcohol to a weighed amount of sodium, we shall note that at first the reaction will be active, but will stop after a while. This is due to the fact that the sodium alcoholate which forms during the reaction covers up the sodium and does not allow the alcohol to reach it any further; thus we obtain less hydrogen than should be the case theoretically.

We have, therefore, worked out the following method for this experiment. Into a small round-bottomed flask *A*, made of good thin glass, we pour 80 to 100 cc. of dry xylene or kerosene, putting into it about two to three grams of sodium. The flask *A* forms a part of the apparatus shown in Figure 3. After having connected the flask with the condenser, we begin to heat it. It must be mentioned that during the heating the part of the apparatus located to the right of the tube containing soda lime must be disconnected. When the xylene begins to boil strongly, the burner is taken away, the flask is quickly taken off, closed with a well-fitting cork (prepared in advance), and immediately wrapped in a towel, after which it is to be shaken violently until it cools. The melted sodium is transformed into very fine dust. When the flask has entirely cooled, it is replaced in the set-up shown in Figure 3 and the calcium chloride tube is connected with the remainder of the apparatus.

Opening the flask slightly we pour into it a known weight of absolute alcohol and connect it quickly with the condenser. The amount of alcohol need not be

equivalent to the amount of sodium, since there is no need to take the sodium into consideration when figuring the volume of hydrogen evolved. Moreover, there should be a calculated excess to prove to the students that even should there be an excess of sodium, it would not replace in the alcohol more than one atom of hydrogen.

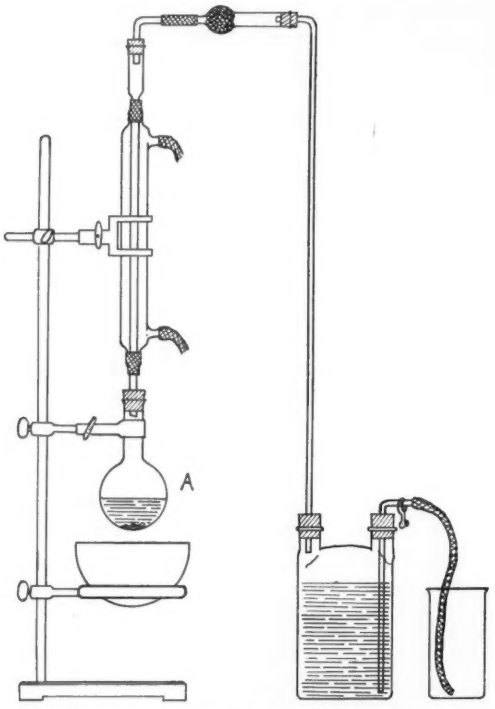


FIGURE 3

By agitation of the flask, the alcohol is brought into contact with the sodium. An active discharge of hydrogen follows and water passes from the Woulfe bottle into the measuring cylinder. When the reaction slows down, the contents of the flask must be brought to a boil. Three to five minutes of boiling suffice to convert all the alcohol into alcoholate. The flask must be left now to cool. It then remains to measure the volume of water displaced and correct the volume of the hydrogen obtained to standard conditions of temperature and pressure. Usually, the results closely approximate the theoretical.

Comparing the results obtained with the quantity of alcohol taken for the reaction, we shall find that in each gram-molecule of alcohol, sodium has replaced only one gram-atom of hydrogen, which is explained by the structural formula we have already deduced.

Thus, the structure of one of the isomeric substances is determined. It remains to examine the structure of the second one, the methyl ether. Since for the compound C_2H_6O only two structural formulas are possible, and since we have proved already that the first is that of ethyl alcohol, it is clear that the second must be ascribed to methyl ether.

If that is the fact then methyl ether must have, for instance, a different behavior toward sodium than has ethyl alcohol. Since we have proved that sodium replaces in the molecule of ethyl alcohol only the hydrogen of the hydroxyl group and since in the formula attributed by us to methyl ether we see that all the six atoms of hydrogen are united with atoms of carbon, we can surmise that not a single hydrogen atom of the molecule of methyl ether will be replaced by sodium.

The apparatus shown in Figure 4 serves to demonstrate that ethyl alcohol reacts with sodium while methyl ether does not.

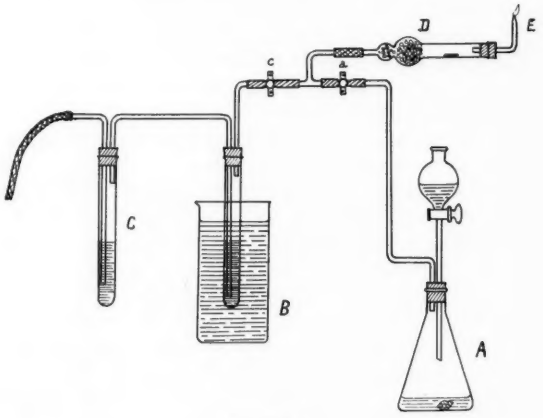


FIGURE 4

A is a small "generator" for producing methyl ether; *B* a test-tube containing alcohol; *C* a test-tube containing concentrated H_2SO_4; *D* a drying tube charged with soda lime. *A* and *B* are connected by means of rubber tubing with a T-tube which in turn is connected with the soda-lime tube. The opening of the latter is closed with a cork through which passes the outlet tube *E*. Opening the clamp *a* (the clamp *c* is closed) we begin to drop the sulfuric acid solution of ether into the water. After the air has been pushed out of the apparatus, the tube *D* is opened for a second and two or three small shavings of sodium, freed of its crust and washed with ethyl ether, are inserted with the aid of pincers. The tube *D* is now closed. The gas emerging from the outlet tube, *E*, can be lighted. Watching the sodium placed in *D*, we shall note that no change takes place in it in the atmosphere of methyl ether. We now extinguish the flame and, first opening the clamp *c* and then closing the clamp *a*, begin to blow air through *C*. The air is first dried by passing through sulfuric acid; then passing through the alcohol it carries along the vapors of the latter, which after entering the tube *D* begin to react with the sodium. This is clearly shown by the changes in the surface of the sodium. One or two minutes after the methyl ether is forced out of the tube *D* we place a test-tube upon the outlet pipe and

collect the hydrogen, the presence of which is proved in the usual way.

In order to prove fully the correctness of the structural formula chosen for methyl ether, we can mention the reaction of methyl ether with hydriodic acid and also the reaction of the synthesis of methyl ether ($CH_3ONa + CH_3I = CH_3OCH_3 + NaI$).

Thus passing under the guidance of the teacher over the whole road of research and testing experimentally the most important points, students obtain a sufficient idea of the actual significance of structural formulas and the method of their deduction. This fully pays for the somewhat lengthy and, perhaps to some extent, difficult method which we propose.

SECOND-YEAR CHEMISTRY FOR HIGH-SCHOOL STUDENTS

WARREN J. HARMAN

Senior High School, Bend, Oregon

THE need for a sound second-year chemistry course in our high schools is becoming more imperative each year. At present our students are literally exposed to a great mass of chemical facts which are not assembled in any logical order and which do not require abstract thinking. Complete memorization of facts is the general practice in most first-year courses in high-school chemistry. Due to this condition, in the main, a large number of otherwise promising research and general chemists are lost to the profession. These students never really find out whether they wish to continue the further study of chemistry.

While it is true that colleges would rather have students untrained in chemistry than filled with the mass of unrelated facts usually offered, the second-year course would enable the superior students really to find themselves and would send much better prepared chemistry students to the colleges. A solid foundation in the theoretical principles of chemistry and a training in abstract thinking would be a boon to the sorely tried college professor.

The writer was confronted with the problem of furnishing instruction in advanced chemistry to a group of high-school pupils who had previously taken the regular course in high-school chemistry. Here was provided an opportunity to test out the value of advanced chemical study in a secondary school. Each of these students was exceptionally well grounded in mathematics and far above average mentally and scholastically.

A suitable textbook of college grade was selected, a course of study mapped out, and instruction started. It was an experiment, so the course was shaped to accommodate this particular group which was planning to make chemistry a life work.

The course was outlined into units, several weeks being devoted to each unit. Laboratory work four hours per week and lectures of one hour three times per week were made the time base of the course.

A. Review—3 weeks
   Valence, equations, oxidation-reduction, chemical arithmetic, and types of reaction.
B. Atomic and molecular weights—2 weeks
   How determined, structure, electron theory, finding formulas of compounds, how used.
C. Basic principles in detail—4 weeks
   Kinetic theory, gases and solutions, equilibrium and ionization in great detail.
D. Elements—3 weeks
   Properties in general. Study of oxygen, hydrogen, and halogens.
E. Periodic law and table—2 weeks
   Value, use, properties of outer and inner groups. Consideration of different tables.
F. Detailed study of groups—10 weeks
   Differences between metal and non-metal. Metallurgy, properties, uses of metals. Consideration of non-metals.
G. Colloidal state—1 week
H. Carbon compounds—4 weeks
   Rather detailed introduction.
I. Introduction to qualitative analysis—3 weeks
   Review ionization and equilibrium.
J. Chemistry in industry—1 week
   Introduce electrochemistry.
K. General review of course—2 weeks

The above course as detailed in outline has proved a success. The students have provided the justification of such a course in their mastery of advanced principles in chemistry and their ability to link theory with laboratory work in the interpretation of experimental findings.

Interest in the second-year course has become so great that a class of fifty would be possible if time and space permitted. There is no better recommendation of the course than this great desire for the inclusion of an advanced class in high school.

The cost of this class has been next to nothing. The students paid a deposit to cover breakage and supplies. The deposit more than covered the cost, thus necessitating no increase in the departmental budget.

Tradition has continually defeated the inclusion of more than one year of chemistry in high school, although two or more years of most other subjects are offered in the curriculum. Because of prejudice in this advance in high-school subject matter, the writer was forced to conduct the advanced class after school under adverse conditions, still further proving that, given a regular place in the curriculum of the high school, second-year chemistry would become one of the most popular and useful courses in high school.

THREE CONVENIENT CHEMISTRY CABINETS

RALPH E. DUNBAR

Dakota Wesleyan University, Mitchell, South Dakota

THE three cabinets illustrated herewith are the outgrowth and result of three very definite needs in our chemistry laboratories. The need in each case will be considered in connection with the purpose and construction of the cabinet. These cabinets were all made in a local planing mill. All are provided with hinged covers or doors with glass, and sturdy, yet inconspicuous locks. Oak wood was used for the main frame and door and three-ply fir for the back in each case. The cost may vary depending upon the materials used, how and where constructed, and the size. These cases were given a stain and varnish coating on the outside to accord with the predominating finish of the rooms, and a coat of soft gray flat paint on the inside. The cost, in any case, is small, and the convenience well worth the effort and expense.

Figure 1 illustrates a display case containing non-returnable articles that are regularly supplied from the chemistry stores. The question of just what articles are listed as non-returnable and their prices arose so frequently that it became something of a nuisance to the storeroom clerk. This cabinet was placed against the wall in a conspicuous position just outside the service window. It measures 20″ by 24″ by 3″ and has been found to be adequate for our purposes. A small card, prominently displayed, states that, "the articles displayed herein are not regularly issued to any student in any of the laboratory courses in chemistry, except upon special request of the student. Once issued, they are non-returnable and are charged to the student at prices indicated."

It soon became equally desirable to display in a prominent location the prices charged for returnable apparatus that might be lost or broken by students while in use. The case illustrated in Figure 2 is the result. It measures 24″ by 36″ by 2″. The inside back surface contains a series of small clips for holding 3″ by 5″ cards in regular rows, arranged in such a way that each series of cards projects some 3″ above the preceding row. In this way one card can be used for listing all similar items, such as the various sizes of Erlenmeyer flasks. When market conditions demand a change in certain prices a new card can be readily prepared without disturbing the listings of any other items. This cabinet is also prominently displayed near the stockroom window. Our experience over a number of years has shown that students usually exercise considerably greater care in the handling of all equipment, with corresponding reductions in breakage charges, where they have this ready access to prevailing prices of all apparatus, returnable and non-returnable.

Numerous organic preparations accumulate in most organic laboratories. While most of these preparations can be used in subsequent experiments, we have long felt a need for some suitable arrangement for

FIGURE 1.—DISPLAY CASE CONTAINING NON-RETURNABLE ARTICLES, WITH PRICES

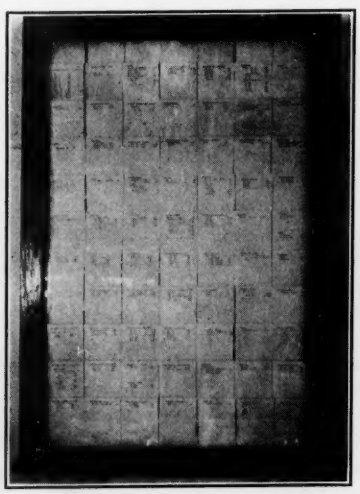


FIGURE 2.—DISPLAY CASE AND RACK FOR TABULATED PRICES OF RETURNABLE APPARATUS

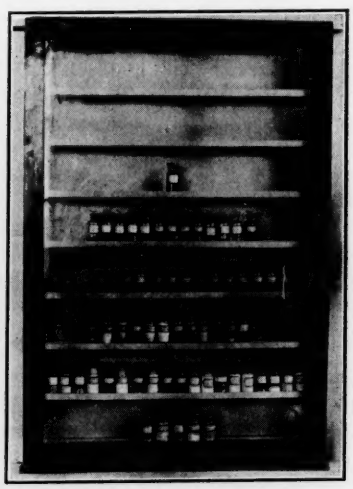


FIGURE 3.—CABINET FOR PRESERVING AND DISPLAYING REPRESENTATIVE ORGANIC COMPOUNDS MADE IN LOCAL LABORATORY

displaying the best and most representative of these products. The case illustrated in Figure 3 is the result. It measures 36″ by 54″ by 5″. This cabinet has been placed in a prominent position in the organic laboratory. Each student is given the privilege of adding products, when in the course of his regular work he can produce a good compound not previously displayed, or can improve upon the quality of one already in the case. Our laboratory assignments in organic chemistry from year to year usually contain a number of optional preparations. It has been interesting to observe the nature of these preparations, selected by most students, in their attempts to make substantial additions to the display or to replace inferior products already present. Most students consistently attempt to complete more than the required number of preparations in order to add something to the display, and yet quality is not sacrificed for quantity, for nothing but relatively pure, attractive, and representative compounds are included. The whole effect has been most wholesome and stimulating and it has been extremely interesting to watch the display grow from year to year.

DEMONSTRATIONS *as a* SUBSTITUTE *for* LABORATORY PRACTICE *in* GENERAL CHEMISTRY

*II. WHAT, WHY, AND TO WHOM SHALL WE DEMONSTRATE?**

HERSCHEL HUNT

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INTRODUCTION

WE MAY be able to convince the partisans of the laboratory method that the discussion-demonstration method gives the college freshmen a broader concept of general chemistry, if we carefully control the experimental proof. We must use both procedures to teach large numbers of students, employing teachers of uniform caliber with equal impetuosity and enthusiasm for the two methods. The same comprehensive examination must then be given to determine the relative achievements of the two groups of students. It will require many years and perfect cooperation to collect such data, and unless the greatest care is used, the experiments may not be decisive. Then, if the demonstration method should prove itself the superior method and in place of an enthusiastic teacher we substitute a supine individual, the mechanism is immediately destroyed.

However, in order to confute the laboratory method, we need only improve what we teach. The scores of laboratory manuals available, dating from 1899 to 1934, are conclusive evidence that teachers have not changed, in this long period of time, what they teach and only minutely how they teach it. This cannot mean that the teachers have not had new ideas. It surely means, first, that the pupils are very limited in their capacity to perform experiments; secondly, that better experiments require laboratory space and equipment that cannot be afforded for freshmen; thirdly, that one individual either has not been sufficiently interested or is not capable of writing a large number of satisfactory exercises. Each of the present-day manuals claims that chemistry is an experimental science, has been developed by experimentation, and therefore can be learned only by experimenting. This beautiful preface is followed by set-ups, experiments, and methods as old as Priestley. With these antiquated experiments, freshmen are left for one year with instructors schooled in the same manner. This condition can be avoided if we equip only the staff, and allow the staff to demonstrate to their classes. The suggested avenue will be limited by the science itself and not solely by finances. With increased enrolments of pupils, who are for the most part immature and inferiorly trained, this condition must prevail. The equipment in the freshman locker of the poor seminary is practically identical with that of the most modern institute of science and technology. One unit for a few hundred students instead of one kit for each student will enable the colleges and universities to build relatively expensive units. Then we can progress with our teaching as we have within our research and industrial processes.

Productive instructors are necessary to organize adequate instruction for a cosmopolitan freshman class. They can develop a group of experiments vastly superior to those now available. The most efficient plan is for the teachers to coöperate in preparing a collection of applicable, recent, thorough exercises for use in demonstrations, rather than for each to try to publish a book of experiments. May someone with the proper

* Contribution to the symposium on The Lecture Demonstration Method vs. Individual Laboratory Work conducted by the Division of Chemical Education at the eighty-ninth meeting of the American Chemical Society, New York City, April 25, 1935.

resources bring about the publication of these exercises. An award might be created for the most meritorious production each year and thereby discourage copyrighted books. Such a scheme would make available to the American youth the best that Americans can produce. Since each demonstrator will explain these in his own personal way, the human element of rugged individualism can be satisfied. The function of this paper is to stimulate progress, progress not held down by our present educational policies and the economics of publishing. The demonstration method allows the professor to adapt the material to the students, rather than the student trying to fit himself to something entirely incompatible with his interests and intellect.

WHAT

I hope the following excerpts will point out the possibilities of the laboratory demonstration method. This hasty (only three years' development) attempt of one individual is, I am sure, a paltry showing compared to what can be made within a year by the combined efforts of my colleagues, should they be given the incentive to create. I am forced, because of space, to omit all comparison and only list those points which I have found by experience to keep the most inadvertent and the most apt freshmen attentive for two or three hours at a period, and to train them as thoroughly as those sent into the laboratory. Many of these experiments are already being used in one form or another in the laboratory, but the significant point is that the average student is not able to execute them properly, so that the correct conclusions are apparent. I have observed that a large proportion of the students in a good class are not sure what happens when they add water to aluminum sulfide. Such outstanding experiences are enough to convince me that someone should be present to speak out what is to be observed and turn and write the conclusions. Of course, this is impossible unless the class is together. Furthermore, the demonstrator can point out wherein he makes his largest error and why it is impracticable to avoid a small percentage error.

All apparatus is put in operational condition before the period opens. However, if the demonstrator sees that he is going to need a little time for manipulating, he first asks the students a question that requires them an equal amount of time to solve. The answer can be heard then or at some more convenient time later. Therefore, we have never found an assistant necessary. A minimum amount of time is spent in routine operations so that the student feels that everything is purely scientific. With all chemicals and apparatus in order and the experiments for the period a unit, the instructor progresses to a climax and conclusions. Almost all the exercises have a null point. Here the students are given a rest period. Some stay and ask questions, others smoke or go for a drink.

I have been questioned about discipline, but since we have had no disciplinary troubles, I have no suggestions to offer on this point. I think this is taken care of by making things interesting.

In order that you may make your own comparison I shall name the exercise as it appears in most manuals and give briefly what changes I have made.

Glass technic: How to cut large tubing, smooth bad ends, make a seal, make a T-tube, bend large tubing, blow a bulb, shape joints for grinding, find pin-holes with Tesla coil, and seal in wires.

Metric System: How to use and care for an analytical balance, determine mass, length, and volume of various objects in English and metric units, read a vernier, and use volumetric glassware.

Gas Laws: Changes in volume with change in temperature and pressure are measured by a set of apparatus capable of giving accurate results. Boyle's, Charles', and Dalton's laws.

Oxygen: How to determine accurately the density of gases, the percentage of oxygen in several compounds, and distinguish between O_2, O_3, and oxides of nitrogen by the fluorescein test. The difficulty of decomposing some oxygen compounds, and the quantitative determination of O_2 by use of pyrogallol, are demonstrated.

Analysis of CuO: How to analyze CuO, data sufficiently accurate to give atomic weight of Cu within 0.1%.

Equivalent and Combining Weight: How to determine the combining weights of many elements, thus giving a broad significance to the term.

Definite Proportions and Atomic Weights: How to determine the formula of CuS from its percentage composition; combining volumes of H_2 and Cl_2.

Water and Hydrates: Analysis of hydrate, kinds of water of chemical composition, and deliquescence.

Solutions: Seeding out, super-saturated, law of partition, and osmotic pressure.

Neutralization: Preparation of standard solutions as in analytical chemistry, choice of indicators, normality by specific gravity of hydrometer reading, and various hydrometer scales.

Ionization: How to measure the conductivity of electrolytes in various solvents.

Freezing point: Determine lowering caused by electrolyte and non-electrolyte using apparatus capable of giving correct result.

Common-ion Effect: Concentration of H^+ by indicator method.

Solubility Product: Rate of reaction of $Pb(NO_3)_2$ with solutions of KI; change in solubility with addition of common ion.

Rate of Reaction: KI and Na_2SO_8 time reactions.

Rate of Reaction: Effect of temperature, pressure, exposed surface, and catalyst.

H_2SO_4: By contact process using Fe_2O_3 as catalyst.

Oxidation-Reduction: Normal solutions made and titrated.

Faraday's Law: Proof by determining amount of Cu, etc., plated out in 30 minutes from proper baths of various metals hooked in series.

Electromotive Series: Measuring actual H_2 electrode against Ag-AgCl, calomel, mercuric oxide, etc.

Ammonia: Properties of NH_3 solutions; test for, using Nessler tubes.

Nitric Acid: Properties of nitrates, test for nitrate, preparation of nitric acid.

H_2S: Use of H_2S and ammonium polysulfide in analytical chemistry.

Complex Ions: Rôle in analytical chemistry.

Carbon Dioxide: Dry ice, properties of water solutions.

Colloids: Protective, charge on, and catophoresis.

Water Softening: Determination of total hardness.

WHY

The tremendous saving of time and money to the student and to the school was pointed out in the Cleve-

land paper.[1] I wish to stress again that a class of students with divergent interests and abilities can be successfully held together by this method so that some do not become discouraged because they are behind. The lectures, recitations, and laboratories are kept parallel easily.

Boys with chemical ability are more likely to be inspired to become chemists if they see the beauty of the science than if they are disgusted by experiments that do not work because of improper apparatus, or that are of little consequence, because they have been made so simple that a poor student can do them. The demonstrator can build his course so that the experiments are in sequence, culminating with the student's having an applicable knowledge of chemistry, not a collection of exercises on preparing inorganic substances, determining qualitatively some property, or collecting data, which, if correct, would prove a principle.

The most often quoted reason for not using discussion-demonstrations is that the student learns little or no technic by observing. I am firmly convinced that the average freshman learns little or no technic by taking the present-day laboratory course. If he does, why is the final exercise no more involved experimentally than the first? I feel that the order of the exercises in the manuals before us is based upon tradition and not an arrangement of increasingly difficult manipulative skills. Psychologists point out that a boy cannot learn to use a lathe more quickly or thoroughly because he has first learned to connect flasks by means of bent glass tubing. If creative work in methods of teaching freshmen chemistry were rewarded we would have young chemists devoting more of their time to their teaching instead of neglecting it for research.

The mortality of freshmen will be decreased, since no penalty is placed on the mind because the hand is unskilful. Many freshmen fail because they cannot solve the problems. What relationship is there between four hours of manual effort in the laboratory each week, and the powers necessary to solve a problem involving solubility product or hydrogen-ion concentration? Let me again remind the defendants of the laboratory method that their defense claims the teaching of skills but they base their grade in the course and the students' achievement largely, if not wholly, on the knowledge of principles. First, we must decide definitely what we are trying to accomplish. If it is knowledge of principles, the discussion-demonstration method is far superior, because an extra recitation is dove-tailed with the laboratory work. Secondly, it is many times easier to discuss a principle with students when one can have their undivided attention, when they all have the same background and are all looking forward to the same experiment, than when they are segregated because one pupil is on experiment three and another has completed the first twelve. One can only confuse a student if one stands at his elbow and chatters while he is busily engaged in becoming a technician by following cookbook directions.

There are numerous technics that a good teacher will use, that, because of space, cannot be written in a book. Many authors realize that there are small differences of opinion and therefore completely omit their point because, after all, it takes many lines to describe the best method of accurately weighing a crucible. Furthermore, it is only human for a student to take lightly a lengthy discussion on a minor point. We are giving our freshmen viewpoints and experiences that we did not come in contact with until we were in a graduate school. We can use our full knowledge by a changeable method, but if the manual bounds the course, we can use mainly the knowledge and experience of its author. We must admit that we have never made freshman manual writing so lucrative as to attract our most fertile minds.

TO WHOM

To chemical majors, chemical engineers, and medical students: Many would-be majors in these fields find that they are mistaken in their choice and change. Many inexperienced students enter college not really knowing in what field they wish to be trained. Granted that a capable student will major in one of these branches of science; if, during the first semester of the freshman year, he is given a broad survey of chemistry by one using correct technic he will be more efficient when placed in the laboratory. Students will develop respect for refined technic and aspire to achieve it only if they can see the benefits of it. Certainly we do not expect freshmen to take pride in apparatus that gives poor results. An individual is not ready to go into an analytical or physical laboratory because he has used a horn-pan balance. However, if he has seen an analytical balance properly used for one year he will proceed carefully and methodically when he takes over one for his own, even though it be his first experience in actually weighing by himself.

All others: The method offers enough more time that we can adapt it so that it will contain chemistry for the lawyer, the merchant, and the farmer. The teacher is informed on what chemistry each craftsman should know, and can stress it; but mere freshmen think that no one outside of a chemistry major should know any chemistry. According to our present manuals the experiments have no application outside the course. This fact alone is enough to create the feeling, "that course is never going to do me any good, so why should I be interested and work hard."

SUMMARY

The marked improvement in content of freshman work, made possible by the demonstration procedure, is stressed. Some exercises are listed which give excellent results. The author feels that the demonstration method gives results which warrant its use with all freshmen.

[1] HUNT, J. CHEM. EDUC., **12**, 73–5 (Feb., 1935).

ELEMENTS *of the* QUANTUM THEORY*

CHAPTER VII—B. VAN DER WAALS' FORCES (CONCLUDED)

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COUPLED LINEAR HARMONIC OSCILLATORS

The behavior of an electron in two neighboring potential boxes is represented, as discussed in the previous sections, by two modes of vibration. Two identical linear harmonic oscillators when coupled together exhibit a similar behavior, and it is by investigating the nature of the interaction of two such oscillators that London has deduced his theory of van der Waals' forces. Before, however, presenting this theory it is necessary to review briefly the concepts, electric moment, and polarizability of molecules.†

An atom of argon or molecule of methane has a symmetrical distribution of electrons about the nucleus or nuclei. That is, the center of gravity of the electrons coincides with that of the positive charges. Such molecules are said to be non-polar. If, however, these molecules are placed in an electric field as, for instance, that produced between the plates of a charged condenser, the positive and negative charges in the molecule are attracted toward the oppositely charged plates, so that the two centers of gravity no longer coincide. If z denote the separation of the two sets of charges, the molecule now behaves like a dipole of electric moment, $\mu_e = ez$. The magnitude of z and consequently that of the induced moment is proportional to the field, F (in volts per cm.), in accordance with the relation,

$$\mu_e = ez = \alpha F \qquad (xii)$$

and the constant α is designated the *polarizability*. The *polarization energy* is therefore given by

$$U_p = -\int_0^{\mu} F d\mu_e = -\int_0^{F} \alpha F dF = -\frac{\alpha F^2}{2} \qquad (xiii)$$

Certain molecules possess an intrinsic electron moment of their own owing to unsymmetrical distribution of charges. In an electric field of strength, F, such molecules will tend to orient in the direction of the field, and the resultant *potential energy* is given by

$$U = -\mu_e F \cos\theta \qquad (xiv)$$

where θ is the angle between the axis of the dipole and that of the field. The negative sign indicates in both equations (*xiii*) and (*xiv*) that the force acting on the dipole is that of attraction.

The field produced by a permanent dipole, at a point along the axis is

$$F = 2\mu_e/R^3 \qquad (xv)$$

where R is the distance of the point from the center of the dipole. At a point on the line perpendicular to the axis of the dipole and passing through the center, the field is given by

$$F = \mu_e/R^3 \qquad (xvi)$$

(These relations are demonstrated in any text on electricity and magnetism.)

Now in an atom, owing to the motion of the electron, we may regard the system as a dipole, of which both the electric moment and direction of orientation are constantly varying. In fact, we may replace the model of an electron in constant motion in the space surrounding the nucleus by three component dipoles, one along each of the three rectangular axes of coördinates. That is, we replace the periodic motion of the electron about the nucleus by three harmonic vibrations (each similar to those of a linear harmonic oscillator) along the three rectangular axes of coördinates, respectively, with the nucleus as origin.

Hence, in order to simplify the problem still further, we shall consider first the interaction of such a single linear oscillator with another identically similar oscillator.‡ As shown in Chapter IV, the S. equation for an oscillating particle moving along one coördinate q is given according to equation (108*a*) by

$$\frac{d^2\phi}{dz^2} + a\left(E - \frac{kq^2}{2}\right)\phi = 0 \qquad (254)$$

where $2\pi\nu_0 = \sqrt{k/\mu}$, and $a = 8\pi^2\mu/h^2$.

This has solutions only for values of the energy given by

$$E_n = (n + {}^1/_2)h\nu_0$$

and the corresponding eigenfunctions are given by

$$\phi_n = \frac{\epsilon^{-x^2/2}}{N_n} \cdot H_n(x).$$

The lowest energy state and associated eigenfunction are, respectively,

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* This is the ninth of a series of articles presenting a more detailed and extended treatment of the subject matter covered in Dr. Dushman's contribution to the symposium on Modernizing the Course in General Chemistry conducted by the Division of Chemical Education at the eighty-eighth meeting of the American Chemical Society, Cleveland, Ohio, September 12, 1934. The author reserves the right to publication in book form.

† The best references for this topic are the following: P. DEBYE, "Polar molecules," Chemical Catalog Co., Inc., New York, **1929**. C. P. SMYTH, "Dielectric constant and molecular structure," Chemical Catalog Co., New York, **1931**.

‡ The discussion in the following section follows closely that given by J. E. LENNARD-JONES, *Proc. Phys. Soc.* (London), **43**, 461 (1931), which is much more comprehensible than that given by F. LONDON.

$$E_0 = h\nu_0/2 \text{ and } \phi_0 = (1/\pi)^{-1/4}\epsilon^{-x^2/2}$$

where $x = 2\pi q\sqrt{\mu\nu_0}/\sqrt{h} = q\sqrt{b}$.

Since

$$1 = \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}\epsilon^{-x^2}dx = \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}\epsilon^{-q^2b}\sqrt{b}\,dq$$

therefore ϕ_0 as a function of q is given by

$$\phi_0(q) = \left(\frac{b}{\pi}\right)^{1/4}\epsilon^{-q^2b/2}$$

Let

$$c = 2\pi^2\mu/h$$

then

$$b = 4\pi^2\mu\nu_0/h = 2c\nu_0$$

and

$$\phi_0(q) = \left(\frac{2c\nu_0}{\pi}\right)^{1/4}\epsilon^{-c\nu_0 q^2} \tag{255}$$

This gives the amplitude of the wave pattern as a function of q, the actual displacement. It will be observed that the transformation from $\phi_0(x)$ to $\phi_0(q)$ has involved a change in the normalizing factor from $(1/\pi)^{1/4}$ to $(2c\nu_0/\pi)^{1/4}$.

If the oscillator is subject to a *uniform electric field, F*, the potential energy term in (254) becomes

$$V = (1/2)kq^2 - eFq$$
$$= \frac{k}{2}\left(q - \frac{eF}{k}\right)^2 - \frac{e^2F^2}{2k}.$$

Thus, if we let $z = q - eF/k$, the wave equation (254) becomes

$$\frac{d^2\phi}{dz^2} + a\left(E + \frac{e^2F^2}{k^2} - \frac{kz^2}{2}\right)\phi = 0 \tag{256}$$

which is of the same form as (254). The energy values however are given by the relation

$$E = (n + 1/2)h\nu_0 - (e^2F^2/2k) \tag{257}$$

That is, the value of ν_0 is unaltered, and $\phi_0(z)$ is identical in form with $\phi_0(q)$, but the whole wave pattern is *displaced* a distance eF/k in the direction of the field. This is similar to the phenomenon which occurs when a molecule or atom is polarized and the *polarization energy* is given according to the last equation, by

$$E_p = -\frac{e^2F^2}{2k} = -\frac{\alpha F^2}{2} \tag{258}$$

where $\alpha = e^2/k$.

Let us now consider the case of *two identical linear oscillators*, each vibrating along the q-axis, with centers a distance R apart. There will be an interaction due to the field produced by each oscillator in the region of the other.

The field produced at oscillator 2 by the vibrating dipole 1 will be given in accordance with equation (xv) by

$$F_1 = 2eq_1/R^3,$$

since eq_1 is the instantaneous value of the electric moment, and the change in potential energy of the second oscillator is therefore

$$V_1 = -eF_1q_2 = -2e^2q_1q_2/R^3 \tag{259}$$

This is, of course, identical with the change in potential energy of the first oscillator due to the field of the second. Thus, V_1 constitutes the *perturbation potential energy* for the system, and the complete S. equation for the coupled oscillators is

$$\frac{\partial^2\phi}{\partial q_1^2} + \frac{\partial^2\phi}{\partial q_2^2} + a\left(E - \frac{kq_1^2}{2} - \frac{kq_2^2}{2} + \frac{2e^2q_1q_2}{R^3}\right)\phi = 0 \tag{260}$$

where ϕ is a function of q_1 and q_2 as well as of R.

This is a type of equation which occurs very often in quantum mechanics, in fact *it is typical of all cases in which there is an interaction between two systems.* We meet with it, in a modified form, in the investigation of the helium atom and of the hydrogen molecule.

Now if the perturbation energy term were not present, the solution of the equation

$$\frac{\partial^2\phi}{\partial q_1^2} + \frac{\partial^2\phi}{\partial q_2^2} + a\left(E - \frac{kq_1^2}{2} - \frac{kq_2^2}{2}\right)\phi = 0 \tag{261}$$

would obviously be obtained by putting

$$\phi(q_1,q_2) = \phi(q_1)\cdot\phi(q_2).$$

For, if we substitute the latter in (261) we obtain the equation

$$\phi(q_2)\left\{\frac{d^2\phi(q_1)}{dq_1^2} + \frac{a}{2}(E - kq_1^2)\phi(q_1)\right\} +$$
$$\phi(q_1)\left\{\frac{d^2\phi(q_2)}{dq_2^2} + \frac{a}{2}(E - kq_2^2)\phi(q_2)\right\} = 0$$

Since $\phi(q_1)$ is a function of q_1 only, and $\phi(q_2)$ of q_2 only, it follows that each of the expressions in large brackets is equal to zero. That is, we obtain the two ordinary differential equations which are each similar to the S. equation for the linear harmonic oscillator. Consequently, the solutions are similar, with the only difference that for q_1,

$$E_1 = (n_1 + 1/2)h\nu_0$$

and for q_2

$$E_1 = (n_2 + 1/2)h\nu_0$$

where $E = E_1 + E_2 =$ total energy and n_1 and n_2 are not necessarily identical.

Thus, for the lowest state of the oscillators, we would have $E = 2E_0 = h\nu_0$, and

$$\phi(q_1,q_2) = \phi(q_1)\cdot\phi(q_2)$$
$$= \{\phi(q_0)\}^2$$

where $\phi(q_0)$ is given by equation (255).

In order to solve equation (260), a "dodge" is employed which changes the equation into one which has the same form as (261). The scheme used consists in a *transformation to two new coördinate variables* defined thus:

$$\left.\begin{aligned} z_1 &= (q_1 + q_2)/\sqrt{2} \\ z_2 &= (q_1 - q_2)/\sqrt{2} \end{aligned}\right\} \quad (262)$$

It will be observed that these relations correspond to a rotation of the coördinate axes through an angle of 45° and are equivalent to the relations

$$q_1 = (z_1 + z_2)/\sqrt{2}$$

and

$$q_2 = (z_1 - z_2)/\sqrt{2};$$

also, that z_1 represents a *mode of vibration* in which q_1 and q_2 are *in phase*, that is, a *symmetrical* mode, while z_2 corresponds to an *unsymmetrical mode of vibration*, since q_1 and q_2 are opposite in phase.

A transformation such as that indicated by the equations in (262) is known as a transformation to *principal coördinates* ("Hauptachsen"). The advantage of such a procedure is evident from the fact that, as a result,

$$\frac{kq_1^2}{2} + \frac{kq_2^2}{2} - \frac{2e^2q_1q_2}{R^3} = \left(k - \frac{2e^2}{R^3}\right)\frac{z_1^2}{2} + \left(k \mp \frac{2e^2}{R^3}\right)\frac{z_2^2}{2}$$

Also it is evident that

$$(dz_1)^2 + (dz_2)^2 = (dq_1)^2 + (dq_2)^2$$

Hence it follows from the rule given in equation (148), for expressing the Laplacian operator in terms of any set of coördinates that equation (260) may be written in the form

$$\frac{\partial^2\phi}{\partial z_1^2} + \frac{\partial^2\phi}{\partial z_2^2} + a\left(E - \frac{k_1z_1^2}{2} - \frac{k_2z_2^2}{2}\right)\phi = 0 \quad (263)$$

where

$$k_1 = k - 2e^2/R^3$$

and

$$k_2 = k + 2e^2/R^3 \quad (264)$$

Equation (263) is evidently separable into two ordinary differential equations, of which the solutions are $\phi_n(z_1)$ and $\phi_m(z_2)$ with the eigenvalues $E_{1,n}$ and $E_{2,m}$ where

$$\begin{aligned} E_{1,n} &= (n + {}^1/_2)h\nu_1 \\ E_{2,m} &= (m + {}^1/_2)h\nu_2 \\ E &= E_{1,n} + E_{2,m} = \text{total energy of system} \end{aligned}$$

and m and n are any two integers (including 0).

The two *new frequencies*, ν_1 and ν_2, are given by the relations

$$\left.\begin{aligned} \nu_1 &= \frac{1}{2\pi}\sqrt{\frac{k_1}{\mu}} = \nu_0\sqrt{\frac{k_1}{k}} = \nu_0\sqrt{1 - 2e^2/(kR^3)} \\ \text{and} \\ \nu_2 &= \frac{1}{2\pi}\sqrt{\frac{k_2}{\mu}} = \nu_0\sqrt{1 + 2e^2/(kR^3)} \end{aligned}\right\} \quad (265)$$

The frequency ν_1, which is less than ν_0, corresponds to that of the symmetric mode, and ν_2 (which is greater than ν_0) corresponds to the frequency of vibration for the antisymmetric mode. Thus the behavior of two coupled oscillators resembles that of the electron in two potential boxes or in the ionized hydrogen molecule. Instead of an energy $2E_1 = h\nu_0$ for the lowest state of the oscillators, we obtain the result, $E = ({}^1/_2)h\nu_1 + ({}^1/_2)h\nu_2$.

Obviously, the transformation to principal coördinates is no longer valid if k is not greater than $2e^2/R^3$. That is, the conclusions involved in (265) are tenable only if $R^3 > (2e^2/k)$, which determines a *lower limit* for the distance R between the zero positions of the oscillators. Since, as shown in equation (258), $e^2/k = \alpha$, the *polarizability*, we can also state this limit in the form $R^3 > 2\alpha$. It should be observed that α may be derived from measurements of dielectric constant or refractive index, and is of the order of magnitude, 10^{-24} cm.^{3}. Thus this theory of interaction of linear oscillators is valid for values of $R > 10^{-8}$ cm. approximately, which corresponds to intermolecular distances.

For the state of lowest energy,

$$\begin{aligned} E &= h(\nu_1 + \nu_2)/2 \\ &= \frac{h\nu_0}{2}\left\{\left(1 - \frac{2e^2}{kR^3}\right)^{1/2} + \left(1 + \frac{2e^2}{kR^3}\right)^{1/2}\right\} \end{aligned}$$

Expanding each term by the binomial theorem, and neglecting powers of R higher than R^{-6}, the result is

$$E = h\nu_0\left(1 - \frac{e^4}{2k^2R^6}\right) \quad (266)$$

Hence, the *interaction energy* is

$$\Delta E = E - 2E_0 = -\frac{e^4}{2k^2R^6}\cdot h\nu_0 = -\frac{\alpha^2h\nu_0}{2R^6} \quad (267)$$

The negative sign shows that the energy arises from *attractive forces* and since the energy varies as R^{-6}, the force of attraction is given by

$$F_A = -\frac{dE}{dR} = -\frac{3\alpha^2h\nu_0}{R^7} \quad (268)$$

That is, the *force of attraction between two pulsating dipoles varies inversely as the seventh power of the distance.* It, therefore, falls off rapidly with increase in distance. Thus, if R is doubled, the force decreases to $({}^1/_2)^7 = {}^1/_{128}$ of its original value.

The behavior of the eigenfunction $\phi(z_1,z_2)$ throws additional light upon the nature of this attractive force between linear oscillators. For the lowest state ($n = m = 0$), it follows from equation (255) that

$$\begin{aligned} \phi(z_1,z_2) &= \phi(z_1)\cdot\phi(z_2) \\ &= \left(\frac{4c^2\nu_1\nu_2}{\pi^2}\right)^{1/4}\epsilon^{-c(\nu_1z_1^2 + \nu_2z_2^2)} \quad (269) \\ &= \left(\frac{\nu_1\nu_2}{\nu_0^2}\right)^{1/4}\left\{\phi_0(q)\right\}^2\epsilon^{-(c\nu_0/k)V} \quad (270) \end{aligned}$$

where $\{\phi_0(q)\}^2$ is the product $\phi(q_1)\cdot\phi(q_2)$ for $R = \infty$ [solution of equation (261)] and V is the perturbing potential energy function, defined by the relation,

$$V = -2e^2z_1z_2/R^3$$

From equation (270) we deduce the probability distribution function for the coördinates of the two oscillators in the form

$$\phi^2(z_1,z_2) = \left(\frac{\nu_1\nu_2}{\nu_0^2}\right)^{1/2}\left\{\phi_0(q)\right\}^4\epsilon^{-(2c\nu_0/k)V} \quad (271)$$

The exponent of ϵ in this equation is given by the expression $4c\nu_0\alpha z_1z_2/R^3$, since $e^2/k = \alpha$, which shows that when z_1 and z_2 are of the *same sign* (the pulsations are *in phase*), $\phi^2(z_1,z_2) > \{\phi(q_1)\cdot\phi(q_2)\}^2$ while for the case when z_1 and z_2 are opposite in phase, the reverse is true.

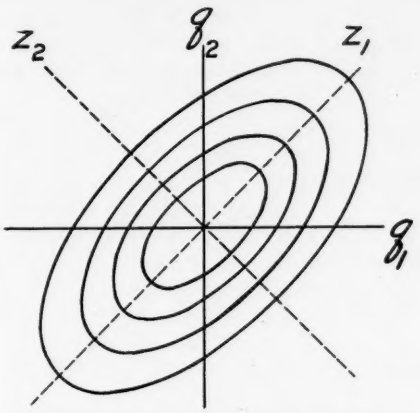

FIGURE 45.—PHASE RELATIONS FOR TWO COUPLED LINEAR HARMONIC OSCILLATORS

"This result," as Lennard-Jones points out,* "can be represented diagrammatically in a two-dimensional space, as shown in Figure 45. The distribution function, being proportional to $\epsilon^{-c(\nu_1z_1^2 + \nu_2z_2^2)}$ [see equation (269)], is like a ridge with its maximum at the origin, and with elliptical contours.† The major axes of the ellipses are $z_2 = 0$, or $q_1 = +q_2$, and the minor axes $q_1 = -q_2$. The corresponding distribution without interaction is a round-topped mountain with circular contours. The probability of finding q_1 and q_2 with the same sign has increased, while that of finding them with opposite sign has decreased. In other words, the interacting dipoles tend on the average to move in phase."

DERIVATION OF VAN DER WAALS' CONSTANT "*a*"

As stated already, the motion of the electron in an atom is actually equivalent to the vibration of three oscillators along the three rectangular coördinates x,y,z. Let us denote by x_1, y_1, and z_1 the component oscillators for one atom and by x_2, y_2, and z_2 the components for a second atom at a distance R. If the z components are chosen to lie along the line joining the atomic centers, then the mutual potential energy of the two sets of oscillators is given by

$$V = e^2(x_1x_2 + y_1y_2 - 2z_1z_2)/R^3 \qquad (272)‡$$

"The probability distribution function," Lennard-Jones writes, "can now be represented only in six-dimensional space. It appears that z_1 and z_2 tend to have the same sign (as before), while x_1 tends to be opposite to x_2, and y_1 opposite to y_2. These are just the configurations for which the oscillators attract. Hence, we may say that two systems tend to interact in such a way that the attraction is a maximum. It is in the generalized sense that we use the expression, 'tend to move in phase,' for actually in this example the x's and y's tend to be out of phase in the usual sense."

The calculation of the van der Waals forces between actual atoms is not a simple matter. But by utilizing equations (267) and (272), it is possible to deduce the magnitude of these forces in the case of hydrogen atoms. From equation (272) it follows that the attraction due to each term x_1x_2, y_1y_2, and z_1z_2 can be treated separately and as shown by H. R. Hassé,** the interaction energy due to each of the first two terms is $^1/_4$ of that due to the z_1 and z_2 oscillators, and therefore equal to $-\frac{\alpha^2h\nu_0}{8R^6}$. Hence, the total interaction energy for a pair of three-dimensional oscillators is

$$\Delta E = -\frac{3}{4}\frac{\alpha^2h\nu_0}{R^6} \qquad (273)$$

Let us now attempt to apply this result to the calculation of the *interaction energy for two hydrogen atoms.*

By investigating the behavior of a Bohr orbit in an electric field it has been shown that the polarizability of the atom is given by $\alpha = \frac{9}{2}a_0^3$, where a_0 is the radius of the orbit.†††

What value of ν_0 can we assign to the electron in a hydrogen atom? Obviously, this "frequency" is a fiction, since, on the basis of the Principle of Indeterminism, no experiment can be devised to determine a frequency of revolution of the electron in its orbit. But when in doubt, it is customary to appeal to a generalization which was enunciated by N. Bohr in the early period of development of his theory, and which is known as the Principle of Correspondence (see Chapter I). According to this principle the behavior of the electrons in an atomic system must approach more and more that predicted by classical physics the higher the quantum number of the orbit. This is equivalent to the statement that when dealing with larger scale phenomena the results deduced by quantum mechanical methods must approximate those deduced by classical mechanics.

In the case of the hydrogen atom, the electronic orbits increase in radius as the ionizing stage is approached. If V_i denote the ionization potential, then the limit of the line spectrum, that is, the maximum fre-

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* LENNARD-JONES, *loc. cit.*, p. 471.

† The equation of an ellipse with respect to rectangular coördinates through the center is $x^2/a^2 + y^2/b^2 = 1$, where a and b are semimajor and -minor axes, respectively. Hence the expression $c(\nu_1z_1^2 + \nu_2z_2^2)$ is constant for all values of z_1 and z_2 which occur on the ellipse whose semiaxes are $1/\sqrt{c\nu_1}$ and $1/\sqrt{c\nu_2}$. Thus, if we have a series of confocal ellipses, as indicated in Figure 45, we can describe any simultaneous combination of values of z_1 and z_2 by stating the serial number of the corresponding ellipse. The use of such coördinates is often very convenient in mathematical problems and has proved useful in dealing with problems of potential.

‡ This relation is readily derived from the equation given in J. H. JEANS's "The mathematical theory of electricity and magnetism," Cambridge Univ. Press, **1908,** p. 368, equation (355).

** HASSÉ, *Proc. Cambridge Phil. Soc.*, **27,** 66 (1931).

††† See P. DEBYE, "Polar molecules," Chemical Catalog Co., Inc., New York, **1929,** Chapter I.

quency of light which can be emitted by the return of an electron to the lowest level, is given by

$$\nu_0 = V_i e/h \qquad (274a)$$

According to electromagnetic theory radiation of this frequency would be emitted by an oscillator having the identical frequency, ν_0. Therefore, we might use in equation (273), the value of ν_0 given by the last equation.

Again, the resonance potential, (V_r), of hydrogen corresponds to the first excited state, and the frequency of radiation emitted because of a transition from this level to the lowest or normal state is

$$\nu_0 = V_r e/h \qquad (275)$$

Since $V_r = V_i(1 - {}^1/_2{}^2) = ({}^3/_4)V_i$, the value of ν_0 is thus confined to the two limits defined by equations (274*a*) and (275).

Now in equation (235) it was shown that the energy of the hydrogen atom in the normal state is given by

$$E_1 = -\frac{e^2}{2a_0}$$

Since $V_i e = -E_1$, the corresponding frequency is

$$\nu_0 = \frac{e^2}{2a_0 h} \qquad (274b)$$

Substituting for α and ν_0 in (273), the interaction energy is found to be

$$\Delta E = -\frac{243}{16} \cdot \frac{e^2}{2a_0} \cdot \left(\frac{a_0}{R}\right)^6$$

$$= \frac{243}{16} \cdot E_0 \left(\frac{a_0}{R}\right)^6 = 15.2\, E_0 \left(\frac{a_0}{R}\right)^6 \qquad (276a)$$

where E_0 is the energy of the normal hydrogen atom. (As may be deduced readily, $E_0 = -13.53$ electron volts.)

From the value for ν_0 given in equation (275) it follows that

$$\Delta E = \frac{3}{4} \cdot \frac{243}{16} E_0 \left(\frac{a_0}{R}\right)^6 = 11.4\, E_0 \left(\frac{a_0}{R}\right)^6 \qquad (276b)$$

Using modified methods (all of them, however, based upon the same fundamental point of view), R. Eisenschitz and F. London,* H. R. Hassé,† and J. E. Lennard-Jones‡ have shown that a more exact value is given by the relation

$$\Delta E = -12.93 \left(\frac{e^2}{2a_0}\right) \left(\frac{a_0}{R}\right)^6 \qquad (277)$$

According to J. C. Slater and Kirkwood,**

$$\Delta E = -12.98 \frac{e^2}{2a_0} \left(\frac{a_0}{R}\right)^6 \qquad (278)$$

which, again, is between the two limits given in equations (276*a*) and (276*b*).

This theory of the origin of van der Waals forces has been applied by F. London, Slater, Lennard-Jones, and others to calculate values of ΔE for more complex atoms and molecules. It remains to describe briefly the manner in which values of the van der Waals constant a may be deduced from values of ΔE.

According to equation (*vii*) a can be calculated if ΔE [$= U(r)$ in that equation] is known as a function of R, the distance between the centers of the molecules (or atoms). On this basis F. London and J. C. Slater have derived the following relations:

(London) $\quad a = 1.13 \times 10^{24}\, \alpha^2 V/b$
(Slater) $\quad a = 1.08 \times 10^{43}\, \alpha^2 \nu^{1/2}/b$

where V is the ionization or resonance potential (in volts), b is the van der Waals constant defined in equation (*viii*) in the first part of this chapter, and ν denotes the total number of valence electrons in the molecule. As will be found by consulting the original publications, values of a calculated by means of these relations have been found to be in satisfactory agreement with values derived from critical constants.

ENERGIES OF CRYSTAL LATTICES

The van der Waals forces of attraction, which, as deduced in the previous sections, vary inversely as the seventh power of the distance between molecules, also account to a large extent for condensation and adsorption phenomena.

London and Lennard-Jones have shown that on this basis it is possible to calculate the energies of sublimation of crystal lattices of such molecules as those of the rare gases, methane, hydrogen, oxygen, nitrogen, and other gases. The present chapter would be incomplete without some discussion of this application of the quantum theory of van der Waals' forces.

The calculation of the energy of sublimation of a lattice involves, as a first step, the calculation of $U(r)$, the potential energy function for a pair of molecules. In equation (*iv*), at the beginning of the chapter, this function was expressed in a general form, involving four constants which have to be determined in any given case from the equation of state of the gas.††† However, on the basis of the quantum mechanics theory, it has been shown that $m - 1 = 6$. In the case of atomic hydrogen, according to equation (273),

$$U(\text{attractive}) = -\frac{3}{4} \cdot \frac{\alpha^2 h \nu_0}{r^6},$$

so that the "attractive-force constant," A, in equation (*iv*) is $6({}^3/_4)\alpha^2 h\nu_0$, and on the basis of equation (277), $A/6 = 6.32 e^2 a_0{}^5$. Substituting the values $e = 4.770 \times 10^{-10}$ electrostatic units, $a_0 = 0.528 \times 10^{-8}$ cm., it is found that $A/6 = 6.04 \times 10^{-60}$ dynes cm.^{6}, and the energy of attraction is $6.04 \times 10^{-60}\, r^6$ ergs, where r is measured in cm.

For the case of helium, the calculation is much more

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* EISENSCHITZ AND LONDON, *Z. Phys.*, **60**, 491 (1930).
† HASSÉ, *loc. cit.*
‡ LENNARD-JONES, *Proc. Roy. Soc.*, **A129**, 598 (1930).
** SLATER AND KIRKWOOD, *Phys. Rev.*, **37**, 682 (1931).

††† Methods of determining these constants are discussed by J. E. LENNARD-JONES in Chapter X of R. H. FOWLER'S "Statistical mechanics," Cambridge Univ. Press.

difficult. According to London,* $A = 7.44 \times 10^{-60}$ dynes cm.^{6}, while Slater and Kirkwood† derive the value $A = 8.94 \times 10^{-60}$ dynes cm.^{6}. For other gases, values of A have been deduced by J. E. Lennard-Jones from the equations of state.

In order to determine $U(r)$ as a function of r, it is necessary to determine the repulsive energy term in equation (*iv*). J. E. Lennard-Jones has determined this empirically from the $PV - T$ data for the gases, on the basis $m - 1 = 6$, and the values of n thus derived vary from 10 to 13.

J. C. Slater and J. G. Kirkwood† have shown that in the case of helium, the repulsive potential energy term may be written in the form

$$U(\text{repulsive}) = Be^{-cr/a_0}$$

where B and c are constants. A similar expression has been deduced by M. Born and J. E. Mayer‡ for the repulsive energy between two ions in a halide lattice. Actually, it makes little difference whether the exponential form is used or the expression of the form r^{-n}, if n is as large as 10. Figure 46** gives the potential energy of pairs of inert gas atoms as a function of their distance apart in Ångstroms (10^{-8} cm.), and it will be observed that owing to the extremely rapid increase in the repulsive force with decrease in distance beyond the equilibrium value (the value of r at the minimum), $U(r)$ increases rapidly in this range. The force at any value of r is of course determined by the *slope* at that point.

* LONDON, *Z. phys. Chem.*, **B11**, 222 (1930).
† SLATER AND KIRKWOOD, *loc. cit.*
‡ BORN AND MAYER, *Z. Phys.*, **75**, 1 (1932).
** J. E. LENNARD-JONES, *loc. cit.*

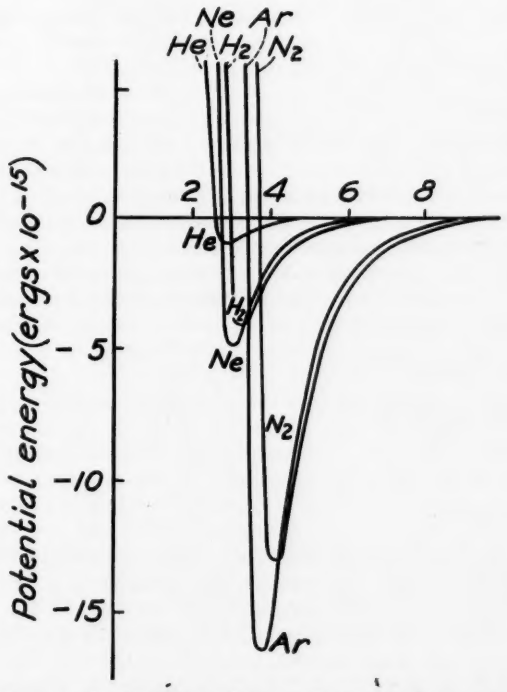

FIGURE 46.—POTENTIAL ENERGY PLOTS FOR PAIRS OF MOLECULES, DUE TO VAN DER WAALS' FORCES

Given $U(r)$ for a pair of molecules it is possible to calculate the total potential energy of all the molecules in a gram-molecular volume of the crystal lattice. The method used may be described as a summation of the energy for every pair of molecules in the lattice. If we denote the total energy by ϕ_0, then

$$\phi_0 = \frac{N}{2}(C_A U_A + C_R U_R) \qquad (xvii)$$

where C_A is the so-called *crystal potential constant*††† for attraction, which depends upon both the value of the attractive force exponent m and the type of crystal lattice, and U_A is the attractive energy term, while U_R designates the repulsive energy term and C_R is the corresponding crystal potential constant (which depends upon the value of n). The factor ($1/2$) is necessary to avoid counting the same atom twice.

The application of the last equation to calculate heats of evaporation may be illustrated by the results obtained for argon. F. London, in his calculation, assumes that the repulsive force exponent, n, $= \infty$, so that $U_R = 0$. For the attractive energy term, U_A, he uses the relation

$$U_A = -\frac{3}{4}\frac{\alpha^2 h\nu_0}{r^6} = 4.92 \times 10^{-59}/r^6 \text{ ergs},$$

where $h\nu_0 = V_i e$, with $V_i = 15.5$ electron volts, and $\alpha = 1.63 \times 10^{-24}$, while r_0 is the minimum distance between atoms.

The observed crystal spacing (minimum distance between atoms) is 3.84×10^{-8} cm., while $C_A = 115.4$. Hence, the energy of sublimation *in calories* is

$$S = \frac{\phi_0}{4.184 \times 10^7} = \frac{N}{2} \times \frac{4.92 \times 10^{-59} \times 115.4}{4.184 \times 10^7 \times (3.84 \times 10^{-8})^6}$$

$= 1715$ calories per mol.

The observed value, according to London, is 2030 cal./mol.

J. E. Lennard-Jones has carried out similar calculations in which the repulsive energy term has been taken into account. It should be mentioned, however, that, in general, the value of the term $C_R U_R$ is small (less than 20%) compared with that of $C_A U_A$. In all cases, the agreement between values of S calculated and those observed is satisfactory. Even in the case of liquids and of many organic compounds, the heats of evaporation may be calculated, with a fair degree of approximation, as the author has observed, by applying equation (*xvii*). Thus it seems most probable that in these cases the forces of cohesion in the solid and liquid state are of the type discussed in the present chapter.

††† Values of these constants for different values of m and n and for various types of lattice structure, are given in Chapter X, FOWLER'S "Statistical mechanics," also by J. E. JONES AND A. E. INGHAM, *Proc. Roy. Soc.*, **A107**, 636 (1925).

On the other hand, in some cases a large fraction of the energy of attraction must be due to the presence of intrinsic dipole moments, as for example in the case of H_2O, $C_6H_5NO_2$, and other molecules for which the electric moment, μ_e, is considerable.

In the case of ionic lattices, such as that of NaCl, the attractive forces are electrostatic, and the corresponding potential energy is given by

$$\phi(\text{Attractive}) = -\frac{N}{2} \cdot C_A \cdot \frac{e^2}{r_0} \qquad (xviii)$$

where r_0 is the minimum distance between ions. The problem of cohesion in such lattices has been the subject of a large number of investigations, and the reader who is interested in following it further will find his efforts well repaid.*

It should be added that the polarizability, α, as well as the proper values of ν_0, necessary for the determination of U_A, may be derived on the basis of wave mechanics from spectral data. However, since such calculations involve the application of the perturbation theory, a discussion of the methods used as well as of other features of the more recent developments of the theory must be postponed for a subsequent chapter.†

* The following references will serve to initiate the student into the extremely voluminous literature on the subject:

M. BORN, "Problems of atomic dynamics," Mass. Inst. Technology, Cambridge, **1926.**

J. SHERMAN, *Chem. Rev.*, **11,** 93 (1932), which contains an excellent review of the whole subject.

J. E. LENNARD-JONES, Chapter X, R. H. FOWLER'S "Statistical mechanics."

† Because of this connection between the van der Waals forces and the spectral dispersion curves, these forces have also been designated *"dispersion forces."* In an interesting paper in *Trans. Faraday Society,* **28,** 316 (1932), M. POLANYI has discussed the application of this theory to the adsorption of gases.

SOME COMPONENT ERRORS *in* DETERMINING *the* VOLUME *of a* MOL *of* OXYGEN

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Beginning students in college chemistry should have some understanding of how component errors may affect a final result. By applying precision of measurement technic, it can be shown that it is often a waste of time to measure a value beyond a certain limit of accuracy. An experiment was conducted to determine the allowable error in measuring a volume of oxygen, knowing the error that will be made in finding its weight, when these two values are used to determine the G.M.V. as in the common laboratory experiment. To measure the volume of oxygen to a greater accuracy than ±10.5 ml. at S.T.P. would be a waste of time. (Apply gas laws to find ± error at laboratory conditions.) The nearest 10-ml. division of a liter graduate would be near enough for a volume measurement considering the error in weight.

ONE of the most valuable tools used in making quantitative measurements is that technic which tells us to what degree of precision related values should be determined. In determining related values, few beginning students realize that observations which are to be brought together in a final relationship do not require the same accuracy of measurement. To carry one determination beyond a certain definite limit which is controlled by the error made in measuring another value would be a waste of time. If a college student were assigned the problem of determining the volume of a long slender cylinder, and the available tools were micrometer calipers that would measure both length and diameter, and a meter stick, how many would choose the correct tool to measure the length?

To bring the problem of precision of measurement before a class in beginning college chemistry, the determination of the volume occupied by a mol of oxygen was chosen as one that involved two related measurements. As this experiment is usually conducted the weight of the oxygen is determined by the loss of weight of potassium chlorate and the volume it occupies by the displacement of water. The weight of the oxygen will be small and its volume will be comparatively large. How precisely should the volume of oxygen be measured considering the error that will always be made in determining its weight?

The determination of the component error in weight was conducted as a class project. A hard-glass test-tube containing the amount of potassium chlorate prescribed by a common manual and one containing potassium chloride were carefully weighed by 24 students. The weights of the two tubes had been previously adjusted so that their difference would be between 1.5 and 2.0 grams. The total weights of the tubes and contents were between 40 and 45 g. To duplicate laboratory conditions two balances were used, but each student weighed both tubes on the same balance. The balance used was a Freshman model sensitive to 1/10 mg. The weights and riders

were in good condition. The students who made the weighings had previously made several other weighings which would certainly place them on an equality with average first-year students throughout the country.

The difference in the weights of the two tubes represents the weight of oxygen heated away. Since it is the loss of weight that is used in the laboratory experiment in determining the gram-molecular volume of oxygen, this difference represents the raw data for calculation of the probable error of a single measurement of weight. All constant, systematic, and accidental errors in the set-up contribute to this final error in weight difference.

Following is the record of loss of weight obtained by 24 students weighing the same test-tubes:

Loss of Weight (Weight of Oxygen)	*Deviation from Average (d)*	*Deviation Squared (d^2)*
1.7010	−0.0094	0.00008836
1.7030	−0.0074	0.00005476
1.7089	−0.0015	0.00000225
1.7009	−0.0095	0.00009025
1.7180	+0.0076	0.00005776
1.7162	+0.0058	0.00003364
1.7148	+0.0044	0.00001936
1.7170	+0.0066	0.00004356
1.7230	+0.0126	0.00015876
1.7159	+0.0055	0.00003025
1.6969	−0.0135	0.00018225
1.6985	−0.0119	0.00014161
1.7251	+0.0147	0.00021609
1.7187	+0.0083	0.00006889
1.7045	−0.0059	0.00003481
1.7070	−0.0034	0.00001156
1.7122	+0.0018	0.00000324
1.7190	+0.0086	0.00007396
1.7019	−0.0085	0.00007225
1.7050	−0.0054	0.00002916
1.7370	+0.0266	0.00070756
1.7058	−0.0046	0.00002116
1.6950	−0.0154	0.00023716
1.7048	−0.0056	0.00003136
41.0501	0.2045	0.00241001
1.7104 Av. Wt.	0.00852 Av. Dev.	

It will be observed that each student obtained a different loss of weight, or weight difference on weighing the same test-tubes. This is, of course, to be expected considering the many small errors affecting all weighings. By taking account of the deviation each student made from the average or best value, it is possible to calculate the probable error or deviation that would be made in determining a single loss of weight. An equation from the mathematics of probability gives the value for the probable error of a single measurement:*

$$\text{P.E.} = \pm 0.6745 \sqrt{\frac{d_1^2 + d_2^2 + d_3^2 + d_4^2, \text{etc.}}{n - 1}}$$

the probable error of a single weighing as calculated from our data is,

$$\text{P.E.} = \pm 0.6745 \sqrt{\frac{0.00241}{23}} = \pm 0.0069 \text{ g.}$$

The equation used to determine the G.M.V. from the weight and volume of oxygen is, G.M.V. $= 32v/w$ where volume (v) is in ml. and weight (w) is in grams.

The error, $\Delta(gmv)_w$, produced in the G.M.V. because of an error, Δw, in making the weighing is,

$$\text{G.M.V.} \pm \Delta(gmv)_w = \frac{32v}{w \pm \Delta w}$$

$$= \frac{32v(w \mp \Delta w)}{(w \pm \Delta w)(w \mp \Delta w)}$$

$$= \frac{32v(w \mp \Delta w)}{w^2 - \Delta w^2}$$

The value Δw^2 may be discarded as the square of a very small number, then

$$\text{G.M.V.} \pm \Delta(gmv)_w = \frac{32vw}{w^2} \mp \frac{32v\,\Delta w}{w^2}$$

$$= \frac{32v}{w} \pm \frac{32v\,\Delta w}{w^2}$$

$$\text{but G.M.V.} = \frac{32v}{w}$$

$$\text{hence} \pm \Delta(gmv)_w = \mp \frac{32v\ \Delta w}{w^2}$$

The error, $\Delta(\text{gmv})_v$, produced in the G.M.V. by an error Δv in measuring the volume v, is calculated similarly:

$$\text{G.M.V.} \pm \Delta(gmv)_v = \frac{32(v \pm \Delta v)}{w}$$

$$= \frac{32v}{w} \pm \frac{32\,\Delta v}{w}$$

$$\pm \Delta(gmv)_v = \frac{\pm 32\,\Delta v}{w}$$

According to precision of measurement technic one error (E) becomes insignificant in comparison with another (e) if it is a little less than half as great, or when

$$0.46E = e$$

Using this relationship we can determine the error in measuring the volume which would be insignificant in comparison with the error made in the weighing, when they are used together in determining the G.M.V.

$$0.46\ \Delta(gmv)_v = \Delta(gmv)_w$$

Substituting the values derived for $\Delta(gmv)_v$ and $\Delta(gmv)_w$ we get,

$$\frac{0.46 \cdot 32\,\Delta v}{w} = \frac{32v\ \Delta w}{w^2}$$

$$\Delta v = \frac{v\ \Delta w}{w.46}$$

Applying this now to our problem, we find the volume which would be occupied by 1.7104 grams of oxygen (the average loss of weight in our data) would be 1196 ml. at S.T.P. The probable error of weight is 0.0069 g. as determined from our data.

$$\Delta v = \pm \frac{1196 \cdot 0.0069}{0.46 \cdot 1.7104}$$

$$\Delta v = \pm 10.49 \text{ ml.}$$

The value for Δv represents the largest error allowable in measuring the volume v when the error in weight loss is ± 0.0069 g.

* WM. S. FRANKLIN, "An elementary treatise on precision of measurement," Franklin and Charles, Lancaster, Pennsylvania, 1925, 27 pp.

The question stated earlier in the article is here answered. It would be a waste of time to measure the volume with great precision, the maximum tolerance being ±10.49 ml. at S.T.P. This error would be larger under laboratory conditions and its increase could be determined by applying the gas laws. Carelessness of observation or sloppiness in laboratory work need not be encouraged by this information, but when it is understood and used intelligently it certainly distinguishes a cookbook worker from a thinking scientist.

A beginning student in college science need not be able to follow the complete technic in finding the tolerance of component errors, but he should know that when two values are being found, one very small and the other comparatively large, the larger one need not be determined with the same precision as the smaller. Advanced students could find the allowable error before making a measurement.

Since in this experiment the total weight of the test-tubes and contents was used to determine the weight difference, it is quite probable that for a smaller difference the probable error of a single measurement would be about the same as here found. In the equation $\Delta v = \frac{v\Delta w}{w.46}, \frac{v}{w}$ is a ratio and would be the same for all values since v and w decrease together. The controlling factor then is Δw, the probable error of a single weight difference. In classes where less accurate balances are used greater errors in volume measurement could be tolerated. The following table shows such a relationship of values:

P.E. of weight of oxygen	*Error in volume which is insignificant at S.T.P.*
±0.005 g.	± 7.60 ml.
±0.007	±10.64
±0.009	±13.68
±0.010	±15.20

NEW INTERPRETATION *of the* IMMEASURABLY FAST REACTION *in a* SOLUTION CONTAINING OXALIC ACID, PERMANGANATE ION, *and* MANGANOUS ION*

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DURING the summer of 1934 the writer was engaged in a search for the interpretation of a puzzling chemical reaction. Reference is made to the well-known fact that in a mixture of oxalic acid, manganous and permanganate ions, an immeasurably fast reaction takes place. The nature of the difficulty will be made clear by a discussion of the quantitative results obtained in certain experiments.

Experiment (*A*): A solution containing 0.0008 *M* $KMnO_4$, 0.1 *M* $K_2C_2O_4$, and 0.125 *M* H_2SO_4 retains its purple color for about five minutes, and its oxidizing titer decreases very little (incubation period). At about this time the color commences to change toward red, with constantly increasing speed, and the oxidizing titer of the solution decreases rapidly (induction period). When the oxidizing titer reaches one-fifth of its original value a new change takes place. The solution is yellow (manganic oxalate complex), and the rate of reaction falls suddenly to a low value. From then on, the reaction continues (end period) until all the manganic oxalate is reduced to manganous ion.

Experiment (*AB*): Another solution, containing 0.01 *M* $MnSO_4$ besides the three substances present in (A), is dark yellow on mixing; the color change is immeasurably fast. The oxidizing titer is the same, within 5%, as that of the parent permanganate solution. In other words, whereas all the permanganate has been reduced to manganic ion, only a small amount of the oxalic acid has been oxidized in this process. From the moment of mixing, the yellow color begins to fade, and the behavior of the solution is similar to that of the yellow solution in the end period of reaction (A). Anticipating a subsequent discussion, we shall consider the behavior of a third type of solution:

Experiment (*B*): A solution, containing all the substances present in solution (AB), except the potassium oxalate, retains its purple color and remains clear

* The present study is a part of a project carried out under a grant from the National Research Council, to which the writer takes pleasure in expressing his obligation.

for about 75 seconds. Only then does its color commence to change toward red. A turbidity appears soon afterward. At the end of 200 seconds the mixture is practically opaque (MnO_2). At the end of 315 seconds the permanganate is completely reduced. The reaction in solution (B) is autocatalytic.

To summarize the observations: in solution (A), containing permanganate ion and oxalic acid, the reaction is slow and autocatalytic. In solution (B), containing acid, permanganate and manganous ions, the reaction is slow and autocatalytic. In solution (AB), containing oxalic acid, permanganate ion, and manganous ion, the reaction is immeasurably fast.

Skrabal[1] offered the following interpretation of the autocatalytic nature of the reaction in system (A): the manganous ion, formed in the main reaction reacts with the permanganate ion, forming manganic ion. The latter in part oxidizes the oxalate ion (hence the name "induction period"), and in part combines with it, forming manganic oxalate complex.

Skrabal extended his interpretation to explain the immeasurably fast reaction taking place in reaction system (AB).[2] The following reaction scheme gives his explanation in its most concise form:

$$Mn(OH)_2 + Mn(OH)_7 \longrightarrow Mn^{+++} \textit{ (weniger rasch)}$$
$$Mn^{+++} + C_2O_4H_2 \longrightarrow Mn(OH)_2 + CO_2 \textit{ (sehr rasch)}$$
$$Mn^{+++} + C_2O_4H_2 \longrightarrow \textit{Komplex (sehr rasch)}$$

The second equation accounts for the small amount of induced oxidation of oxalic acid. The sum of the first and the third equations supposedly accounts for the immeasurably fast change of the permanganate to manganic oxalate complex.

Skrabal's interpretation has been accepted as a working hypothesis during the past thirty years. Thus, as late as 1932, Launer[3] in a criticism of Skrabal's mechanism for the end period in reaction system (AB) accepts his interpretation of the rapid initial reaction, in which the manganic oxalate is formed.

Considering that the net reaction in reaction system (AB), which Skrabal's scheme is supposed to explain, is immeasurably fast, Skrabal's mechanism could only be correct if the first reaction in his scheme is immeasurably fast. As far as the writer is aware, Skrabal did not carry out an experiment of type (B), in which the oxalate ion is omitted. The results of experiment (B) show conclusively that Skrabal's interpretation cannot be maintained without a modification. For, how can a very slow reaction be the initial step in an immeasurably fast complex reaction?

It is commonly stated that manganous ion catalyzes the reaction between permanganate and oxalic acid. In describing the results of experiment (AB) it was stated that only a small amount of oxalic acid was oxidized in the immeasurably fast initial reaction. In view of this it would appear that it is more correct to consider oxalate ion as a catalyst in the reduction of permanganate with manganous ion. Looking at the problem from this angle, the writer noticed a similarity between this case and three other cases of catalysis of the permanganate-manganous ion reaction in acid solutions.

In an investigation of the mechanism of the slow reaction between permanganate and manganous ions* it was observed that fluoride and sulfate ions accelerated the reduction of the permanganate. It was found, furthermore, that the rapid reaction between permanganate and thiosulfate ions in acid solution was radically changed if manganous ion was added before the thiosulfate ion. This was surprising at first, considering that the reaction of manganous ion alone with permanganate is slow. However, the results fitted into a simple interpretation if it was assumed that, just as in the case of oxalate ion, the thiosulfate catalyzed the manganous-permanganate reaction and that the product of this reaction immediately oxidized the thiosulfate ion.

Thus one of the objectives of this investigation was to find the mechanism whereby oxalate, fluoride, sulfate, and thiosulfate ions catalyze the manganous ion-permanganate reaction in acid solution. Attention is called to the fact that the first three ions are known to form complexes with manganic ion. It is fairly safe to assume that manganic ion also forms a complex with thiosulfate ion, which is analogous to the red ferric thiosulfate complex, except that it is even less stable.

A clue to a plausible explanation of the catalysis by complex-forming ions is contained in a recent paper. Launer and Yost[4] produce conclusive evidence that Skrabal's mechanism for the reaction taking place during the middle period in a reaction system of type (A) cannot be correct. They offer another mechanism which seems to be in quantitative agreement with the observed rates. In their mechanism Launer and Yost assume that the permanganate ion is in *rapid* equilibrium with Mn^{4+}, Mn^{3+}, and Mn^{++}. This assumption, if extended to reaction systems of type (B) and (AB), offers a simple and highly plausible explanation of the observed results.

When manganous ion is added to an acidified solution of potassium permanganate, a rapid equilibrium is established, in which the concentrations of Mn^{4+} and of Mn^{3+} are extremely small. The quadrivalent manganese has a tendency to hydrolyze, forming manganese dioxide or its hydroxide, but this reaction is slow in acid solutions. Solid manganese dioxide catalyzes the further precipitation of this substance.

If oxalate ion is also present, the equilibrium is

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[1] SKRABAL, *Z. anorg. Chem.*, **42**, 1 (1904).

[2] SKRABAL, ref. 1, pp. 58, 74; *Z. Elektrochem.*, **40**, 653 (1905); *Sammlung chemischer und chemisch-technischer Vortrage*, **13**, 343 (1908).

[3] LAUNER, *J. Am. Chem. Soc.*, **54**, 2597 (1932).

* The results of this investigation are reported by the author in *J. Phys. Chem.*, **39**, 1057–66 (Nov., 1935). It has been mentioned previously that the reaction is autocatalytic. Manganese dioxide is responsible for the autocatalytic nature of this reaction. A probable explanation is offered at the end of this paper.

[4] LAUNER AND YOST, *J. Am. Chem. Soc.*, **56**, 2571 (1934).

shifted at once, and the permanganate ion is rapidly reduced, forming the manganic oxalate complex. If thiosulfate ion is present, then the permanganate is rapidly reduced to manganic thiosulfate complex, but the latter is unstable and is reduced at once to manganous ion. Finally, both fluoride and sulfate ions catalyze the manganous ion-permanganate reaction because of their tendency to form the respective manganic complexes.

SUMMARY

1. The reduction of permanganate ion with manganous ion in acid solution is autocatalytic. The reaction is catalyzed by manganese dioxide.

2. It is shown that Skrabal's mechanism for the immeasurably fast reaction between permanganate, manganous, and oxalate ions, in acid solution, cannot be maintained without a modification.

3. It is shown that the assumption of a *rapid* equilibrium between permanganate, manganous ion, quadri-, and trivalent manganese ions offers a complete explanation of the rapid reaction mentioned in (2). The same assumption explains the accelerating effect of other complex-forming ions on the manganous ion-permanganate reaction. The same assumption had been used by others to interpret the reaction between oxalic acid and permanganate in the absence of manganous ion.

CHEMISTRY LIST FOR PUBLIC LIBRARIES

ONE by-product of the eighty-eighth meeting of the American Chemical Society was the library list of popular books on chemistry prepared by Mr. Ward, Technical Librarian of the Cleveland Public Library, with the coöperation of the Cleveland Section, and published in leaflet form. The list includes the following titles, together with brief descriptive comments upon each volume:

INTRODUCING CHEMISTRY AND ITS WORKS

*Clarke, B. L. Marvels of modern chemistry. 1932.
Findlay, Alexander. The spirit of chemistry. Rev. ed. 1930.
*Holmes, H. N. Out of the test tube. 1934.
Kendall, James. At home among the atoms. 1929.
*Philadelphia College of Pharmacy and Science. Popular science talks.
*Sadtler, S. S. Chemistry of familiar things. Rev. ed. 1930.

CHEMISTRY IN COMMERCE AND INDUSTRY

Egloff, Gustav. Earth oil. 1933.
Howe, H. E., ed. Chemistry in industry. 2 v. 1924–25.
Leith, C. K. World minerals and world politics. 1931.
Little, A. D. The handwriting on the wall. 1928.
Mantell, C. L. Sparks from the electrode. 1933.
Read, T. T. Our mineral civilization. 1932.
Redman, L. V. and Mory, A. V. H. The romance of research. 1933.
*Slosson, E. E. Creative chemistry. Rev. ed. 1930.
*Spring, L. V. W. Non-technical chats on iron and steel. Rev. ed. 1927.

ORGANIC AND LIFE CHEMISTRY

Chamberlain, J. S. Chemistry in agriculture. 1926.
Deming, H. G. In the realm of carbon. 1930.
Parsons, T. R. Materials of life. 1930.

CHEMISTRY THROUGH THE CENTURIES

*Beery, P. G. Stuff; the story of materials in the service of man. 1930.
Jaffe, Bernard. Crucibles. 1930.
Krantz, J. C., ed. Fighting disease with drugs. 1931.
Thompson, C. J. S. Lure and romance of alchemy. 1932.
Weeks, M. E. Discovery of the elements. 1933.

* Titles marked with a star (*) are suggested for first reading.

Copies of the leaflet, for which the expense of printing was defrayed by the Cleveland Section, may be had upon application to the Technical Department, Cleveland Public Library, for the cost of postage only.

CORRESPONDENCE

ADJUSTED CORRECTIONS FOR BURET READINGS

To the Editor

DEAR SIR:

In applying corrections to measurements of any kind, blunders are more frequently made when the sign of the correction is negative than when the sign is positive.

In volumetric analysis the use of negative corrections to buret readings may easily be avoided by expressing all the corrections as positive quantities. This is done by subtracting (algebraically) from each correction the value of the largest negative correction, using the remainder as the adjusted correction. To illustrate, suppose the first and second columns are obtained by the usual methods:

Buret Readings	*Preliminary Corrections*	*Adjusted Corrections*
0.00	0.00	+0.03
10	−0.01	+0.02
20	−0.02	+0.01
30	−0.03	+0.00
40	−0.02	+0.01
50	−0.01	+0.02

By subtracting −0.03 from each preliminary correction the adjusted values in the third column are obtained.

Since the volume delivered from a buret is found by subtracting the first reading from the second, the use of the adjusted corrections gives the same result that is obtained by using the values in the second column.

UNIVERSITY OF FLORIDA
GAINESVILLE, FLORIDA

HUBERT G. SHAW

MATHEMATICAL PROBLEM PAGE

Directed by EDWARD L. HAENISCH

Montana State College, Bozeman, Montana

IN ORDER that a function $u = f(x, y)$ be a maximum or minimum the following conditions (*Lagrange's criterion*) must be satisfied.

$$\frac{\partial u}{\partial x} = 0;\ \frac{\partial u}{\partial y} = 0;\ \frac{\partial^2 u}{\partial x^2} \cdot \frac{\partial^2 u}{\partial y^2} - \left(\frac{\partial^2 u}{\partial x\,\partial y}\right)^2 > 0$$

When $\frac{\partial^2 u}{\partial x^2}$ is negative, u is at a maximum; when it is positive, u is at a minimum.

If a differential, $du = Mdx + Ndy$ has been produced by the differentiation of a known function, $u = f(x,y)$, $M = \left(\frac{\partial u}{\partial x}\right)_y$ and $N = \left(\frac{\partial u}{\partial y}\right)_x$. It is further true that

$$\frac{\partial M}{\partial y} = \frac{\partial^2 u}{\partial y \partial x} = \frac{\partial N}{\partial x} = \frac{\partial^2 n}{\partial x \partial y}$$

Such a differential is known as an *exact differential*. The function u can be obtained from $Mdx + Ndy$ by the integration of Mdx, considering y as a constant, followed by the integration of those terms in Ndy which do not contain x. u is the sum of the results of these two integrations.

Integration gives:

$$\int (Mdx + Ndy) = u(x,y) + c$$

$$\int_{x_1y_1}^{x_2y_2} (Mdx + Ndy) = u(x_2,y_2) - u(x_1,y_1)$$

The value of the integral depends only on the initial and final values of the variables and is independent of the path followed between these two points. When $Mdx + Ndy$ is inexact, integration can be effected only by the assumption of some relation between y and x; *i. e.*, a definition of the path between the initial and final values. The difference between exact and inexact differentials is extensively used in thermodynamics.

REFERENCES

DANIELS, p. 193.
MELLOR, pp. 77, 298.

PROBLEMS

1. Examine the function $x^3y^2\,(1 - x - y)$ for maxima and minima.

2. Divide a number C into three parts so that the product of these three parts is a maximum.

3. Find the relation which must exist between the initial concentrations a and b so that the velocity of the bimolecular reaction shall be a maximum.

$$V = \frac{dx}{dt} = K(a - x)(b - x)$$

4. Which of the following differentials are exact? Obtain u where possible.

$$du = e^x \sin y\,dx + e^x \cos y\,dy$$
$$du = V^n\,dp + np V^{n-1}\,dV$$
$$du = (x^2 - axy + y^2)dx + (y^2 + xy - ax^2)dy$$

5. Find the value $\int_{0,0}^{4,3} (2xydx + x^2dy)$. Show that the value of $\int_{0,0}^{1,1} (ydx + xdy)$ depends on the relations chosen between y and x. Choose $y = x^2$ and $y = x^3$.

6. The first law of thermodynamics is $dQ = dU + pdV$. Consider the internal energy $U = f(T,V)$. Show that

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV.$$

For a perfect gas $\left(pV = RT;\ \left(\frac{\partial U}{\partial V}\right)_T = 0\right)$ show that dQ is an inexact differential while dQ/T is an exact differential.

SOLUTIONS TO DECEMBER PROBLEMS

1. $du = \cos(x + y)\,dx + \cos(x + y)dy$
$du = yx^{y-1}\,dx + x^y \ln x\,dy$
$du = (ye^x + e^y)dx + (e^x + xe^y)dy$

2. $\frac{\partial u}{\partial x} = 3x^2y^2 + 4y^4$ $\qquad$ $\frac{\partial u}{\partial y} = 2x^3y + 16xy^3$

$\frac{\partial^2 u}{\partial y \partial x} = 6x^2y + 16y^3$ $\qquad$ $\frac{\partial^2 u}{\partial x \partial y} = 6x^2y + 16y^3$

$\frac{\partial u}{\partial x} = e^x \sin y$ $\qquad$ $\frac{\partial u}{\partial y} = e^x \cos y$

$\frac{\partial^2 u}{\partial y \partial x} = e^x \cos y$ $\qquad$ $\frac{\partial^2 u}{\partial x \partial y} = e^x \cos y$

3. $du = 0 = (3x^2y + y^2 - y)dx + (x^3 + 2xy - x)dy$

$$\frac{dy}{dx} = -\frac{3x^2y + y^2 - y}{x^3 + 2xy - x}$$

4. $U = f(T, v)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dv$$

The third variable, p, has been kept constant so we may write

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$$

The substitution of this value into the equation for C_p gives

$$C_p = \left(\frac{\partial U}{\partial T}\right)_v + \left[\left(\frac{\partial U}{\partial v}\right)_T + p\right]\left(\frac{\partial v}{\partial T}\right)_p$$

$\left(\frac{\partial U}{\partial T}\right)_v = C_v$; for a perfect gas $\left(\frac{\partial U}{\partial v}\right)_T = 0$;

from $v = \frac{nRT}{p}$, $\left(\frac{\partial v}{\partial T}\right)_p = \frac{nR}{p}$.

$$C_p = C_v + [0 + p]\frac{nR}{p}$$

$$C_p - C_v = nR$$

for one mole of gas $C_p - C_v = R$.

THE SELECTION OF TITRATION UNKNOWNS

CHARLES R. CONARD

Harvard College, Cambridge, Massachusetts

IN A COURSE open to students presenting chemistry for college entrance we have an experiment on titration. In addition to the usual comparison of solutions and the determination of the concentration of an "unknown solution," each student determines the equivalent weight of a solid acid. The selection of these solids has been a little difficult, for we wanted them to be inexpensive, inert enough to be packaged in paper envelopes (2–4 grams), stable enough to keep from year to year, unaffected by atmospheric moisture and, finally, soluble enough in water to allow fairly rapid titration.[1]

We have found that the following substances answer these specifications and give good results in the hands of inexperienced students.

Substance	*Formula*	*Equiv. wt.*
Succinic acid	$C_2H_4(CO_2H)_2$	59
Oxalic acid*	$(CO_2H)_2 \cdot 2H_2O$	63
Citric acid	$C_3H_4(CO_2H)_3$	64
Malic acid (dl)	$C_2H_3O(CO_2H)_2$	67
Phthalic anhydride*	$C_6H_4(CO)_2O$	74
Tartaric acid	$C_2H_2O_4(CO_2H)_2$	75
Sodium acid sulfite	$NaHSO_3$	104
Furoic acid	$HOC_4H_3CO_2H$	112
Potassium acid sulfite*	$KHSO_3$	120
Sodium acid sulfate	$NaHSO_4$	120
Potassium acid sulfate*	$KHSO_4$	136
Sodium acid phosphate	$NaH_2PO_4 \cdot H_2O$	138
Salicylic acid	$HOC_6H_4CO_2H$	138
Potassium acid tartrate	$KHC_4H_4O_6$	188

The substances are listed in order of their equivalent weights to show that considerable duplication of values occurs. As a consequence of this duplication we had less than half of the number of different values we desired. In case there is a choice of compounds of nearly the same equivalent weight the best substance is indicated with an asterisk. Malic and furoic acids are the least satisfactory of the substances listed, but, unfortunately, duplication occurs at other values.

In order to obtain additional equivalent weights we have tried admixture with diluents. This imposes further limitations on the properties of the substances employed. The acid must be of low equivalent weight in order to keep the equivalent weight of the mixture within reasonable limits (we set 200 as a maximum). Furthermore, the substance should not cake after being powdered.

We have worked with malic, citric, oxalic, and succinic acids, and as neutral material we have used sugar or potassium chloride. Malic and citric acids absorbed water or caked too much to allow thorough mixing of the powdered materials. Oxalic acid, at first, seemed satisfactory. However, both the samples mixed with sugar and those mixed with potassium chloride turned brown on standing over the hot summer months, and in some cases a black sticky tar had formed. Although the oxalic acid mixtures apparently remain unchanged for several weeks at 20°C., the change takes place in a few hours at 45°C.

The mixtures of succinic acid and potassium chloride, however, are quite stable to any atmospheric changes in temperature and humidity. The mixtures may be prepared by sifting the powdered materials through a 40-mesh sieve, weighing the individual components to the desired accuracy, mixing them by pouring from one paper to another several times and, finally, sifting the mixture again before bottling. Results within 2 per cent. of the correct value were given full credit, since the burets employed frequently caused more than 1 per cent. error.

By choice of the relative amounts of the acid and salt any equivalent weight above 59 may be obtained. The weight relationships are expressed by the following equation,

$$E_m = 59\left(\frac{1 + W_s}{W_a}\right)$$

where E_m is the equivalent weight represented by the mixture; 59 is the equivalent weight of pure succinic acid; W_s is the weight of salt; and W_a is the weight of acid used in preparing the mixture. E_m may be conveniently plotted against W_s/W_a to construct a graph from which the relative amounts of material necessary for a given equivalent weight may be read at a glance.

[1] Additional considerations have been discussed by M. G. MELLON AND J. P. MEHLIG, "Problems of teaching quantitative analysis. I. Analyzed samples," J. CHEM. EDUC., **11**, 664–6 (Dec., 1934).

A. T. Burtsell
F. B. Dains
Tenney L. Davis
J. Howard Graham
B. Clifford Hendricks
J. W. Howard

ABSTRACTS

R. A. Baker, *Abstract Editor*

D. C. Lichtenwalner
Greta Oppe

C. M. Pruitt
Leopold Scheflan
E. D. Walter
E. Roger Washburn
Sidney Weinhouse
G. H. Woollett

KEEPING UP WITH CHEMISTRY

Drying heavy leather in five hours. T. K. Sherwood and L. E. Garono. *Chem. & Met. Eng.*, **42,** 539 (Oct., 1935).—Wet leather to be dried is coated with a thin layer of kieselguhr—water paste. The water is drawn by the strong capillary pull of the kieselguhr coating into the wet paste, evaporating at the outer surface of the coating. Tannin substances in solution are deposited on the surface of the coating. The coating is later removed. It is possible thus to dry leather at temperatures as high as 180°F. without discoloration or other injury of the product. Sole leather bends are dried in this way at 156°F. in $5^1/_2$ hours in a commercial dryer. This is a 97 per cent. reduction in drying time of the older methods. J. W. H.

Bakelite's anniversary. J. A. Lee. *Chem. & Met. Eng.*, **42,** 540–3 (Oct., 1935).—From a small rented building with a second-hand steam engine and a 40 gal. still to a vast modern plant covering 125 acres with a capacity of 50,000,000 lb.; from a new product for which a market had to be found to a series of products for which there is a demand from almost every known industry the world over is the record of the Bakelite Corporation in a 25-year period. J. W. H.

Burlap bags for bulk chemicals. R. W. Lahey. *Chem. & Met. Eng.*, **42,** 544–7 (Oct., 1935).—Burlap bags occupy a humble position in the packing world. They are used whenever powdered or lump materials are packed, for they are one of the cheapest and most durable packages that can be chosen. Burlap bags made from jute are more universally used in the chemical industry than cotton bags because they can be obtained at a lower price for equal strength. In those instances where cotton bags are used, it is largely to prevent the slight contamination that may occur from jute fiber. The weight of the burlap, the twist of the yarn, and the manner of the weaving are the chief elements in the strength of the cloth. J. W. H.

The electric lamp. J. T. Randall. *Sch. Sci. Rev.*, **16,** 480–9 (June, 1935).—A history of the incandescent lamp, and a discussion of its principles and manufacture. S. W.

Will Uncle Sam's gas tank run dry? A. E. Talbert. *Sci. News Letter*, **28,** 234–6 (Oct. 12, 1935).—Petroleum experts including geologists, chemists, and statisticians are in wide disagreement regarding a gasoline shortage in the United States within the next five or six years. Dr. Benjamin T. Brooks, consulting chemical engineer, and L. C. Snyder, geologist, both of New York, predict a serious shortage as soon as 1940–43. Such a shortage would be a national calamity, skyrocketing the price of motor fuel, bringing into use "Tom Thumb" automobiles, and handicapping navy and air forces of the United States. Securing gasoline from other than current sources could scarcely stave off such a shortage if it comes upon us within such a short period. Substitutes such as alcohol and Diesel oil are too expensive to be considered unless the price of gasoline soars to levels four or five times the present price. Dr. J. Gustav Egloff, a Chicago petroleum expert, on the other hand, asserts that there is a petroleum reserve in the United States which would supply us for ten or fifteen years without even considering our secondary supply of three or four times that of the reserve supply. Specialists of the Petroleum Administrative Board, the Geological Survey, and the Bureau of Mines consider the reserve supply sufficient to last at least fourteen years if no new fields were discovered. Newly discovered oil is being added each year about equivalent to two-thirds of that year's consumption so that the prospect is that it will be longer than a fourteen-year period before the gasoline drought begins. However, it is important that something be done about it even if it is pushed ahead a decade or more. Shale oil holds promise in the quest for more gasoline. Alcohol may come to the rescue as a dilutant of natural gasoline. Hydrogenation of coal may prove to be another way of providing this fluid fuel for gas motors. However, none of these substitutes are competitors with natural gasoline at the present because of their much higher cost. B. C. H.

The lead content of human tissues and excreta. S. L. Tompsett and A. B. Anderson. *Biochem. J.*, **29,** 1851–64 (Aug., 1935).—An accurate method for the estimation of Pb in human tissues, blood, and excreta is described.

Pb was found in all tissues examined. The average concentrations in mg. of Pb per kg. for adults were: liver 1.73, kidney 1.34, spleen 1.68, brain 0.5, rib 8.55, vertebra 7.09. Tissues from a case of known exposure to Pb showed higher figures, especially the rib, with 119 mg. per kg.

The average daily excretion of Pb by 10 patients was 0.05 mg. for urine and 0.22 mg. for feces.

Blood obtained from 3 normals and 18 patients gave values of 40–70γ per 100 cc., with an average of 55γ.

A case of plumbism in a solder maker showing very high concentrations of blood Pb is reported. E. D. W.

Hemicellulose from oat hulls. E. Anderson and P. W. Krznarich. *J. Biol. Chem.*, **111,** 549–52 (Oct., 1935).—Extraction of oat hulls with a 5% solution of NaOH gave a mixture of hemicelluloses. The yield was about 28% of the weight of the hulls used. After hydrolysis of the hemicelluloses with a 4% solution of H_2SO_4 the sugars *d*-xylose, *l*-arabinose, and a compound of *d*-glucuronic acid with 2 molecules of *d*-galactose were found present. E. D. W.

Darkness by the tank car. Anon. *Ind. Bull. Arthur D. Little, Inc.*, **105,** 2 (Oct., 1935).—Carbon black, the soot made by burning natural gas in multitudes of small flames directed against specially constructed metal channels, is the subject of this article. Until recently almost all carbon black of the world was made in Texas and Louisiana, and to a lesser extent in Oklahoma and Wyoming. Now Japan produces an appreciable amount and attempts are being made to use Russian and Roumanian natural gas; but few other countries can follow their example. In this country, our annual production is now about 300,000,000 pounds, of which over 80% goes to rubber manufacturers here and abroad. Carbon black is truly "the life of the rubber tire," as no other substance has been found which imparts to the tire such tensile strength, ability to withstand wear, and resistance. The original method of producing carbon black was to compress it into blocks which could be shipped, but they were dirty to handle and expensive to transport in bags. By a new process of stirring or churning, the spongy mass is freed of part of its air and is rolled into minute spheroidal particles to a density of 20 pounds per cubic foot and shipped in special tank cars which convey it much as though it were a liquid. To date about ten million pounds have been shipped in this manner. There are special types of carbon black, called "Thermatomic black" and "Gastex." These are made by cracking processes whereby a gas is decomposed in contact with hot surfaces rather than during partial combustion. These types are valuable for use in rubber but not as pigments. G. O.

Reinforced paint films. Anon. *Ind. Bull. Arthur D. Little, Inc.*, **105,** 3–4 (Oct., 1935).—Paint and varnish films tend to grow brittle with age. Modern high-intensity pigments give but little mechanical aid in strengthening paint films, for the pigments are ground exceedingly fine to give the utmost covering power. For some few years aluminum powder has been used in primers and for other purposes where its silvery color was either useful, or at least not objectionable, for making dense, tough, and impenetrable films because of its "leafing" property which forms a deposit of overlapping scales. Besides aluminum and bronze metallic powders, commercial use is made of finely divided graphite and talc. For strictly decorative purposes, fish scales are used as well as a chemical substitute for these. The paints containing metals are not desirable around electrical fixtures and machinery.

Bronze powders do not withstand acids well and aluminum is affected by alkalies. Mica is an ideal flaky material for this purpose, but in order to use mica it was necessary to find the best way to grind it so that it would produce flakes with smooth edges that would leaf together. Another problem that had to be solved was the chemical treatment of the flaked mica to make it wettable and to rid it of staining impurities. A product called "Aratone" is now available. It is the scrap of high-grade India mica from the electrical industry, and its decorative possibilities are enhanced by a dyeing technic which produces flakes in many brilliant colors. G. O.

Boron carbide, a new abrasive. O. REICHARDT. *Chem.-Ztg.*, **59**, 602–3 (July 24, 1935).—Boron carbide is made from B_2O_3 and coke at 2500–2600°C., in a special oven; its formula is B_4C. It is harder than carborundum and therefore is exceeded in hardness only by the harder grades of the diamond. It is also better than carborundum in its higher resistance to pressure, toughness, and conductivity of the electric current. L. S.

The identification of radio-elements artificially produced by means of neutrons and applications in chemistry as indicators. O. ERVACHER AND K. PHILIPP. *Angew. Chem.*, **27**, 409–14 (July 6, 1935).—A review. *A.* Identification of artificial radio-elements: 1, Chemical identification; 2, Physical identification. *B.* Manufacture of artificial radioactive atoms: 1, Sources of neutrons; 2, Manufacture of radioactive atoms which are isotopic with the radiating element; 3, Manufacture of radioactive atoms which are not isotopic with the radiating element. 21 references. L. S.

The preparation of guanidine nitrate from ammonium thiocyanate. H. GOCKEL. *Angew. Chem.*, **27**, 430 (July 13, 1935).—All methods known depending upon the reaction

$$2NH_4SCN = H_2S + CN_3H_5 \cdot HSCN$$

yield only up to 38.8% of the guanidine base. The new method shown by the equation

$$NH_4SCN + Pb(NO_3)_2 + 2NH_3 = PbS + CN_3H_5 \cdot HNO_3 + NH_4NO_3$$

is nearly quantitative and can be carried out at a much lower temperature than the others. Detailed directions are given. This method makes it possible to convert NH_4SCN cheaply into the more valuable guanidine. This may lower the price of guanidine sufficiently to make it usable as a nitrogen fertilizer (over 40% N_2). L. S.

The chemical tourist visits Wyandotte, the city built upon salt. W. HAYNES. *Chem. Industries*, **37**, 333–7 (1935).—Beneath Wyandotte, Michigan, lie vast beds of solid rock salt and upon these deposits have been built two great chemical plants, Michigan Alkali and Pennsylvania Salt, and clustered about them are half a dozen other chemical operations. This chemical group is the industrial nucleus about which the city has grown. Today the city of Wyandotte, with a population of 28,000, stretches along the Detroit River for five miles, a busy, depression-proof community where trim, modern stores and block after block of well-kept attractive homes bear evidence of the importance of this chemical center.

Among other plants and products in Wyandotte is Sharples Solvents Corporation, who make amyl alcohol by hydrolyzing chlorinated pentane. They make six of the seven possible amyl alcohols, and amyl acetate, the amyl amines, tertiary amyl phenol, and amyl mercaptan. The latter is the prize "inverted perfume" and serves wonderfully well as an indicator of leaks in gas lines when used at the rate of $^7/_{10}$ of a pound to a million cubic feet of natural gas. Also there is the Bakelite subsidiary, Halowax, producing synthetic waxes by the chlorination of naphthalene; and the Michigan Oxygen Sales Co. supplying oxygen for welding to the motor car factories of the Detroit district.

The mother plant of this interesting group dates back to 1898, when the Pennsylvania Salt Manufacturing Co. purchased 130 acres, overlying enormous salt beds. They built an electrolytic plant which has grown to the largest operation of this process in the Middle West. The packing of lye is an important part of the plant operation but no longer the most important. The chlorine is put to work in a whole series of processes resulting in muriatic acid, bleaching powder, carbon tetrachloride, ferric chloride including the new anhydrous form. A low-pressure ammonia plant consumes the hydrogen gas from the alkali-chlorine cells. At the giant plant of the Michigan Alkali Works there has been a parallel development where excess carbon dioxide from the lime kilns is compressed to the solid form in blocks. A. T. B.

Points for pyrethrum buyers learned by pyrethrum growers. R. E. CULBERTSON. *Chem. Industries*, **37**, 341–4 (1935).—Eight years of experimental work by the author with pyrethrum on several hundred plots in 24 states shows conclusively that pyrethrum can be grown successfully in the United States. In the areas suitably located, the plants hold up and yield well, and the flowers are as high, and, in many instances, higher in toxicity than those imported. From the viewpoint of the insecticide manufacturers using pyrethrum, information of value has been developed. A. T. B.

APPARATUS, DEMONSTRATIONS, AND LABORATORY PRACTICE

Colour reactions in the micro-chemical determination of minerals. J. ADAM WATSON. *Min. Mag.*, **24**, 21–34 (Mar., 1935).—"The solution to be tested is contained in a small test-tube, and one drop is placed by means of a small pipet either in a cavity of a spotting-plate or on a filter paper. A drop of the reagent is then added and the color observed. When it is necessary to treat the test solution prior to the actual testing this treatment is carried out in a watch-glass, the solution being filtered if necessary. In the main the development of a color on adding the reagent is sufficient to indicate whether an element is present. Some few of the reactions here described gave stains with more than one element, and it is necessary to treat the stain further to see whether either or both are present, or the original solution may be specially treated and retested."

The extremely simple apparatus and technic employed are described.

"When dealing with substances that are soluble in water or in *dilute* hydrochloric acid it is quite sufficient to prepare a weak solution in either of these liquids. In no case is it necessary to have a solution stronger than 0.5%. Strong hydrochloric acid may be employed if it gives a clear solution of the substance, but the excess of acid must be removed before the tests are applied, since in many cases a strong acid interferes with the reactions. Most minerals, however, will not give with either of these methods a solution that can be relied upon to contain all the elements originally present. The most satisfactory way to treat an unknown mineral is to fuse a small quantity of the finely powdered material with sodium carbonate in a loop of platinum wire. Complete decomposition is obtained by adding to the fused bead a small quantity of sodium peroxide. When metals which alloy with platinum are suspected the mineral powder should be mixed with the sodium carbonate before preparing the bead. The fused bead so obtained is treated with distilled water in a watch-glass and the liquid decanted or filtered from any insoluble material."

"By the treatment outlined here the aqueous alkaline solution may contain the major quantity of the following elements: Na, K, B, Al, Si, Sn, P, V, As, Sb, S, Cr, Mo, W, Cl, F; while the acid solution may contain similarly: Cu, Ag, Au, Mg, Ca, Ba, Sr, Cd, Hg, Ti, Pb, U, Mn, Fe, Co, Ni. Certain elements may appear in both solutions; among these are Sb, As, etc."

Reagents required

Alizarine: saturated solution in alcohol, add HCl till yellow, dilute with equal volume alcohol, and filter.

Alizarine S: 0.1% solution in water.

Ammonium mercury thiocyanate: 9 g. $(NH_4)CNS$, 8 g. $HgCl_2$. 100 cc. water.

Ammonium molybdate: 5 g. $(NH_4)_2MoO_4$, 100 cc. water (dissolved cold), then add 35 cc. HNO_3 (density 1.2).

Ammonium persulphate: solid.

Aniline: aniline hydrochloride dissolved in concentrated HCl.

Benzidine: 0.05 g. benzidine dissolved in 10 cc. glacial acetic acid, dilute to 100 cc. with water.

Dihydroxy tartaric osazone: solid.

Dimethyl-amino-benzal rhodanine: 0.03% solution in acetone.

Dimethylglyoxime: 1% in alcohol.

*Diphenyl carbazide: 1% in alcohol.

*Diphenyl carbazide thiocyanate: saturated solution in cold alcohol. Saturate with KCNS and add crystal of KI.

Diphenyl thiocarbazone (dithiazon): 0.002% in carbon tetrachloride.

Hydrogen peroxide: 20 vols.
Mercuric nitrate: 10% $Hg(NO_3)_2$ in 1% HNO_3.
β-Nitroso-α-naphthol: 2 g. dissolved in 100 cc. glacial acetic acid and diluted with 100 cc. water.
Potassium bichromate: solid.
Potassium chromate: 1% in *N* acetic acid.
Potassium ferrocyanide: 2*N* solution.
Potassium iodide: *N* solution.
Potassium thiocyanate: 2*N* solution.
Phosphomolybdic acid: 5% solution.
Sodium cobaltinitrite: solid.
*Sodium rhodizonate: 5% solution.
Thiourea: 10% solution.
Titan yellow: 0.1% solution.
Turmeric: 20 g. turmeric extracted with 50 cc. alcohol, filtered, and diluted with 50 cc. water.
Zinc uranyl acetate: 10 g. uranium acetate dissolved in 6 cc. of 30% acetic acid by heating. Dilute to 50 cc. with water. 30 g. zinc acetate dissolved in 3 cc. of 30% acetic acid. Dilute to 50 cc. Mix two solutions, add trace of NaCl, allow to stand 24 hours. Filter.
Acetic acid: 2*N*
Hydrochloric acid: concentrated and *N*/10.
Nitric acid: *N*.
Phosphoric acid: concentrated.
Oxalic acid: *N*.
Sulfuric acid: concentrated.
Sodium hydroxide: 5 *N* and *N*/10.
Ammonia solution: concentrated.
Ammonium carbonate: 5 *N*.
Ammonium chloride: saturated.
Ammonium phosphate: 5 *N*.
Ammonium sulfide: concentrated.
Barium chloride: *N*.
Copper sulphate: *N*/100.
Mercuric chloride: saturated.
Potassium chromate: *N*.
Potassium cyanide: 5 *N*.
Potassium nitrite: *N*.
Sodium acetate: saturated.
Sodium carbonate: anhydrous.
Sodium peroxide: solid.
Sodium phosphate: 2*N*.
Sodium thiosulphate: *N*.
Silver nitrate: *N*.
Stannous chloride: *N* in concentrated HCl.
Starch: solid.
Zinc granulated (free from arsenic): solid.
Magnesium powder: solid.
Zinc sulphate: *N*.

N = Normal solution containing the molecular weight of the salt in 1000 cc. of water.

All solutions are made in distilled water unless another solvent is indicated. Alcohol used is 90% industrial spirit.

For further details the original article should be consulted.

*Solutions of these reagents do not keep well and should be made up as required.

Element	*Reagent*	*Apparatus*	*Method of applying test*	*Color*
Na	Zinc uranyl acetate	Watch-glass	1 drop solution, 1 drop Am_2S, 1 drop Am_2CO_3, filter, neutralize, 5–6 drops reagent. stir.	Yellow
K	Sodium cobaltinitrite	Watch-glass	1 d. soln., 1 d. acetic acid, few grains solid reagent, warm.	Yellow ppt.
Cu	$Am_2Hg(CNS)_4 + ZnSO_4$	Porc. dish	1 d. soln., 1 d. Am_2HPO_4, acidify conc. H_2SO_4, 1 d. $ZnSO_4$, 1 d. reagent, warm.	Violet red
Ag	K_2CrO_4	Spot plate	1 d. soln., 1 d. reagent, 1 d. acetic acid.	Red
Au	$SnCl_2$ + HCl	F. paper	1 d. soln., 1 d. reagent, I d. KCNS, boil in water.	Purple
Mg	Titan yellow	Spot plate	1 d. soln., 1 d. Am_2S, warm, filter, 1 d. reagent, 1 d. NaOH.	Pink
Ca	Dihydroxy tartaric osazone	Watch-glass	1 d. soln., 1 d. Am_2S, warm, filter, few grains reagent.	White ppt.
Sr	Sodium rhodizonate	F. paper	1 d. soln., 1 d. K_2CrO_4, 1 d. reagent on edge of spot.	Brown
Ba	Sodium rhodizonate	F. paper	1 d. soln., 1 d. reagent, 1 d. dil. HCl.	Brown
Zn	$Am_2Hg(CNS)_4 + CuSO_4$	Porc. dish	1 d. soln., 1 d. Am_2HPO_4, acidify H_2SO_4, 1 d. $CuSO_4$, 1 d. reagent, warm.	Violet
Cd	Diphenyl carbazide thiocyanate	Spot plate	1 d. reagent, 1 d. soln., 1 d. AmOH.	Violet
Hg	Dimethyl-amino-benzal rhodanine	F. paper	1 d. soln., 1 d. HCl, 5 d. Na_2HPO_4, filter on paper, 1 d. reagent on edge.	Pink
B	Turmeric	Porc. dish	1 d. reagent, 1 d. soln., 1 d. HCl, evap. to dryness, 1d. NaOH.	Green
Al	Alizarine S	Spot plate	1 d. soln., 1 d. NaOH, boil, filter, 1 d. reagent, 2 d. acetic acid.	Pink
Tl	Potassium iodide	Spot plate	1 d. soln., 1 d. reagent, 1 d. $Na_2S_2O_3$.	Yellow
Si	Am_2MoO_4 + benzidine	Porc. dish	2 d. reagent, 1 d. soln., warm, 2 d. oxalic acid when cold, 1 d. benzidine, 2 d. Na acetate.	Blue
Ti	Hydrogen peroxide	Spot plate	1 d. soln., 1 d. H_3PO_4, 1 d. reagent.	Yellow
Zr	Alizarine + HCl	Spot plate	1 d. soln., 1 d. HCl, 1 d. reagent.	Violet
Sn	Phosphomolybdic acid	F. paper	1 d. soln., 1 d. HCl, few grains Mg powder, transfer to filter paper, 1 d. reagent.	Blue
Pb	Dithiazon	Spot plate	1 d. soln., 3 d. KCN, 1 d. AmCl, 1 d. reagent. (Run blank.)	Pink
P	Am_2MoO_4 + benzidine	Porc. dish	2 d. reagent, 1 d. soln., 1 d. benzidine, 2 d. Na acetate.	Blue
V	Aniline	F. paper	1 d. reagent, 1 d. soln. containing HNO_3.	Green
As	Gutzeit reaction	Sp. appar.	.....	Black
Sb	Phosphomolybdic acid	F. paper	1 d. reagent, 1 d. soln., warm.	Blue
Bi	Thiourea	Spot plate	1 d. soln., 1 d. reagent, 1 d. HNO_3.	Yellow
Cr	Diphenyl carbazide	Spot plate	1 d. soln., 1 d. H_2O_2, 1 d. AmOH, warm on watch-glass, acidify H_2SO_4, transfer, 1 d. reagent.	Violet
Mo	KCNS + $SnCl_2$	F. paper	1 d. conc. HCl, 1 d. soln. in center, 1 d. reagent, 1 d. $SnCl_2$. (Color on edge.)	Red
W	KCNS + $SnCl_2$	F. paper	1 d. conc. HCl, 1 d. soln. in center, 1 d. reagent, 1 d. $SnCl_2$. (Color in center.)	Blue
U	$K_4Fe(CN)_6$	F. paper	1 d. soln. in watch-glass, 4 d. $Na_2S_2O_3$, transfer to-filter paper, 1 d. reagent on edge.	Brown
SO_4	Mercuric nitrate	Porc. dish	1 d. soln., 1 d. reagent, evap. nearly to dryness, 2 d. water.	Yellow
Mn	$Am_2S_2O_8 + AgNO_3 + H_3PO_4$	Porc. dish	1 d. soln., 1 d. $AgNO_3$, 1 d. H_3PO_4, few grains solid $Am_2S_2O_8$, warm.	Purple
F	$SiO_2 + H_2SO_4$, etc.	Sp. appar.	.....	Blue
Cl	$K_2Cr_2O_7 + H_2SO_4$	Sp. appar.	.....	Violet
I	Starch paste	Spot plate	1 d. soln., 1 d. reagent, 1 d. KNO_2.	Blue
Fe	Potassium thiocyanate	Spot plate	1 d. soln., 1 d. reagent, 1 d. HCl.	Red
Co	β-nitroso-α-naphthol	Spot plate	1 d. soln., 1 d. AmCl, 2 d. AmOH, boil, 2 d. water, filter, 2 d. H_3PO_4, 1 d. KI, 2 d. $Na_2S_2O_3$, filter, 1 d. reagent.	Brown
Ni	Dimethylglyoxime	F. paper	1 d. soln., 1 d. H_2O_2, heat spot on paper, 1 d. reagent on edge.	Pink

O. R.

RECENT BOOKS

THE BACKGROUNDS AND FOUNDATIONS OF MODERN SCIENCE. An Integration of the Natural Sciences for the Orientation of College Freshmen. *Richard E. Lee*, A.M., M.Sc., Sc.D., Professor of Chemistry and Director of the Freshman Course in Science in Allegheny College. The Williams & Wilkins Company, Baltimore, 1935. xxv + 536 pp. (53 blank pages.) 13.8 × 21.4 cm. 20 illustrations. 12 tables. $4.00.

This book attempts the difficult task of supplying to young students, not yet expert in any branch of science, a synoptic view of science as a whole, what it is in its method, its origins, and its development, what it has learned, what man amounts to, what he knows—to the end that the student may discover his own position in the order of things and, having basis for judgment, may develop a sense of values and find in positive knowledge a guide for conduct. The author has used a preliminary edition of the book for three years in classes of from two to three hundred students. The following quotations from the preface indicate his point of view.

"An effort is made to organize the major conceptions of science in a manner which will enable the student to develop insights. . . . New insights, not merely *more* of what he has had, are required to motivate the freshman inaugurating his college course. The beginnings of a true appreciation of science are coeval with glimpses of it as an intellectual technique devised by man to serve social ends; as a demonstrated way of knowing; as a mode of thought; as a way of looking at the universe in the effort to rationalize and manipulate environment; as a great public storehouse of social knowledge in terms of which the individual may find at least a partial interpretation of countless daily experiences, etc. A broad basis of insights rather than an accumulation of unrelated facts about this and that is productive of a rational synoptic outlook. . . .' The objective of this book is the orientation of the student. . . .

"Man has always wanted a 'picture' of the universe that he might loosen the bonds of Nature and discover his 'prospects' and significance. Thus, he is introduced to the student as both a 'scientist' and a 'philosopher.' Consciously or unconsciously, he has been striving to formulate a few fundamental conceptions or 'first principles' in terms of which he might describe or symbolize the universe. Thus man is conceived as a 'universe-builder.' In the corridor of universes running from Thales to Einstein are found the 'pictures' of the conceptions of the universe which have been dominant at various periods during a span of 2500 years. . . .

"In viewing scientific knowledge as being constituted of interlocking systems of correlated and subordinated facts rooting into a few primary concepts, the student easily arrives at a conception of the *unity* of science. . . .

"A continuous historical background is presented to the end that the growth of science through the centuries may be reviewed in terms of incidents, intellectual outlooks, or personalities. It is believed that such procedure will enable the student to attain a background of culture now necessary to all walks of life. . . .

"The 'scientific method' is definitely an intellectual technic. The craftsman should be familiar with his tools."

The book is divided into five parts: Part I. Introduction: Adjustment and Techniques (two chapters); Part II. Man's Major Techniques: Scientific and Philosophic (four chapters); Part III. Development of Modern Scientific Techniques (seven chapters); Part IV. Historical Backgrounds of Man's Techniques (seven chapters); and Part V. A Special Study of Various Aspects of the "Primary Stuff" of the Universe (ten chapters). The fifth part, "wherein the student collaborating in the writing of a book needs resort to the *experimental* or *scientific method* as well as to a 'recall and integration' of previously acquired facts," contains 53 blank pages for written exercises.

The account of chemistry appears to be good, and the experiments are well chosen to illustrate the important principles. Physics and astronomy are described in terms of the latest developments. Students will be impressed with the wonder of it all, but one questions whether they will be able to assimilate it and to place its parts in proper perspective. How can students be expected to answer questions to which the best informed men of science can give no answer? such questions, for example, as this (page 516), "Account for the positively charged fountain-pen handle after it was rubbed with a woolen cloth." If a student thinks that he can answer the question, it will be because he has no notion at all of cause and effect or of what it is that constitutes an explanation. One wearies of the author's vocabulary, of techniques, and stuff, and universe-builders (what of universe-understanders?), of his too frequent use of italics and of quotation marks around unusual words, of his use of the word, social, in accordance with the prevailing vogue of the New Deal, where another word would convey the meaning more exactly. Science is certainly not "a great public storehouse of social knowledge"; science is your positive knowledge, my positive knowledge, everybody's knowledge, public positive knowledge, but social knowledge is summarized in treatises on sociology as chemical knowledge is summarized in treatises on chemistry. Nor is science "an intellectual technique devised by man to serve social ends." If it is an intellectual technic, then surely it serves whatever intellectual ends man has. Let us be reasonable in our socialism.

The author's account of the method of science is weak, and his descriptions of the various philosophical doctrines are inadequate or misleading.

Professor Lee's book is one to be chewed and digested, chewed by those with strong teeth and digested by those whose gastric juices are potent. We doubt whether freshmen can handle it. Perhaps they may think that they digest it, more's the pity; perhaps they become like the senior about to graduate from college whose admiring fiancée, invited for Commencement Day, remarked to him, "Well, it must be wonderful now to know everything." "Yes," he replied, "it is." A very proper use of Professor Lee's book would be in a graduate seminar by students who had already acquired the things which are supposed to constitute a liberal education. It would polish them up, tie their ideas together, and make them educated. The more one knows, the more, we believe, he will find in the book to question, and the more to stimulate him. It would be a good book for every teacher of science to read and chew thoroughly.

The book is clearly printed and well put together. Except for the Christian name of Avogadro, we have noted no typographical errors.

TENNEY L. DAVIS

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POPULAR SCIENCE TALKS, SEASON OF 1934. Presented by members of the faculty of the Philadelphia College of Pharmacy and Science, and published under the auspices of the American Journal of Pharmacy, Volume XII, edited by *Ivor Griffith*, P.D., Ph.M., Sc.D., Philadelphia College of Pharmacy and Science, Philadelphia, Pa., 1935. 198 pp. 15 × 23 cm. $1.00.

For the past nine years the Popular Science Lectures by the Philadelphia College of Pharmacy and Science have been published, and the volumes sold at cost as part of the educational program of the College. As a reservoir of interesting information they have proved useful to high-school students and teachers, librarians, and those called upon to make luncheon and club talks on science.

The contents for Volume XII: "The Herbs and the Stars," by Charles H. LaWall; "Conquest of the Planet Earth," by George Rosengarten; "Living Light," by Arno Viehoever; "Tooth Truths," by Ivor Griffith; "Free Air," by Arthur Osol; "Famous Finds by Pharmacists," by John Kramer; "The History and Romance of Microscopy," by Louis Gershenfeld; and "Silver, Metal of the World," by Clifton C. Pines.

As one would expect in such a collection of popular lectures, there are wide differences in merit. "The History and Romance

of Microscopy," and "Living Light" appear as the more scholarly, while "Tooth Truths" and "Famous Finds by Pharmacists" will appeal more to the high-school student's delight in the Ripley "Believe It or Not" facts.

There are serious typographical errors on pages 86, 114, and 198. More illustrative material would add to the attractiveness of the volume to the layman, but as long as the price of one dollar is held, it will be impossible to expand in this direction.

FURMAN UNIVERSITY
GREENVILLE, SOUTH CAROLINA JOHN R. SAMPEY

CHEMISTRY GUIDE AND LABORATORY EXERCISES, with Accompanying Tests. *Martin V. McGill*, Lorain High School, Lorain, Ohio, and *G. M. Bradbury*, Montclair High School, Montclair, N. J. Revised edition of CHEMISTRY WORKBOOK AND LABORATORY GUIDE by the same authors. Lyons and Carnahan, Chicago, 1935. ix + 374 pp., incl. appendix. 31 figs. 19 × 26.5 cm. detachable punched. $1.00.

This workbook and laboratory guide is definitely organized on the unit basis. The sixteen units treated are: The World, Air, Water, Formulas, Ions, Equations, Sulfur, Halogens, Nitrogen Family, Colloids, Carbon, Organic Chemistry, Metallurgy, Useful Compounds, Aluminum and Iron, and Other Metals. Each unit contains (1) an illustrated overview, (2) study outline and assignments, including time allotment, (3) several problems, (*a*) reviewing known facts, (*b*) illustrative experiments, (4) summary review, (5) suggested projects, (6) additional topics for discussion, (7) topics for honor reading and reports.

The foreword by Prof. B. S. Hopkins of the University of Illinois states that this edition "retains all of the tested features of the earlier chemical workbook." Cautions are conspicuously printed. The pupil is insistently reminded to keep the problem before him. Emphasis is placed on learning by doing in the laboratory.

The laboratory directions are clearly and concisely stated. No elaborate apparatus is required for them. The quantitative experiments are well chosen. Sixty-five experiments serve the needs of either college preparatory or general classes in chemistry.

The exercises give the pupils ample opportunity to drill on problems, formulas, and principles. Since many of the exercises are objective, the checking need not consume too much of the instructor's time.

The general make-up of the book is excellent, and it can be made to lie flat on the desk top when opened. The size of type of subscript numbers in the formulas might be made larger to save eyestrain.

Oxidation-reduction reactions are considered in terms of electron transfer. Electron transfer is not so extensively applied to replacement, ionization, or electrolytic cells. Double replacement reactions and those of neutralization are considered in the conventional manner.

The book is designed to supplement any introductory chemistry textbook. It is full of interest-getting devices. The *Guide* is a valuable aid to both pupil and teacher. The wide use of the previous edition forecasts an even more extended use of the improved volume. It should be carefully considered by all teachers of introductory chemistry. ELBERT C. WEAVER

BULKELEY HIGH SCHOOL
HARTFORD, CONN.

THE BIOCHEMISTRY OF THE LIPIDS. *Henry B. Bull*, University of Minnesota. Burgess Publishing Company, Minneapolis, Minn., 1935. v + 127 pp. 47 figs. 21 × 27 cm. Mimeoprint. $3.25.

This book represents the best concise and up-to-date reference on the lipids which is available. The author has compiled in good form the most significant data available concerning the physical and organic chemistry of the simple and complex lipids. Graphs, tables, equations, and graphic formulas have been used freely. Journal references are given in the text for the more important recent sources of information. In approximately one-fifth of the book an excellent outline is given of what is known and conjectured by leading investigators about the physiology of the lipids in both animals and plants. There are more typographical errors than usual in a reference text, but these do not comprise a serious factor in the value of the monograph. There is no index, but the table of contents is given in sufficient detail to serve this purpose fairly satisfactorily for an advanced student. The mimeoprinting on one side of each page only is clear and neatly arranged.

THE UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA C. G. KING

DOCTORAL DISSERTATIONS ACCEPTED BY AMERICAN UNIVERSITIES, 1934–1935. *Donald B. Gilchrist*, Editor. The H. W. Wilson Company, 950–72 University Ave., New York City, 1935. 102 pp. Paper, $1.00.

This is the second of these annual lists, compiled for the National Research Council and the American Council of Learned Societies, by the Association of Research Libraries; Donald B. Gilchrist, editor.

No list of similar scope has previously appeared for American dissertations, although complete lists for French and German university dissertations have been published annually for many years.

Of the many dissertations accepted each year only about one-third ever appear in print. Also universities now make it an almost universal practice to file full manuscript theses in duplicate, and to make copies available through inter-library loan. For these reasons this publication is a necessary one.

In form, the list is very similar to, and continues, the annual list in the field of science, issued since 1920 by the National Research Council. Its scope has been broadened to cover all fields of study; and that there may be no break in the statistical record, the dissertations in the field of science have been classified in the same subject groups used in the N.R.C. series, those for other fields being selected on much the same basis.

For greater convenience, the list has been arranged in seven main divisions: Philosophy, Religion, Earth sciences, Biological sciences, Social sciences, Literature, and Art. While the arrangement is an arbitrary one, it follows in a general way the organization of American universities into divisions and departments, and the finding of material is further facilitated by a general subject cross-index and an author index. When theses appear in print, mention of this fact is made also.

Each annual number contains, as supplementary material, records of previous theses lists, annual lists of doctoral dissertations in progress, statistical tables showing doctorates in science according to subject, and distribution of doctorates by university by subject. There is also a table showing the present practice in all universities whose theses are listed, as to the publication and loaning of their own dissertations.

THE CRACKING ART IN 1934. U. O. P. Booklet No. 165. *Gustav Egloff* and *Emma E. Crandal*. Universal Oil Products Co., 310 S. Michigan Ave., Chicago, Ill. 196 pp. 15 × 23 cm.

This report covers publications from December 1, 1933, to January 1, 1935. The table of contents is as follows:

I—Introduction
II—Status of Cracking
III—Economics of Cracking
IV—Cracking Outside the United States
V—The Cracking Reaction
VI—Liquid Vapor Phase Cracking
VII—Vapor-Phase Cracking
VIII—Combination Liquid-Vapor and Vapor-Phase Cracking
IX—Cracking with Oxidation
X—Electrical Cracking
XI—Combination of Operation
XII—Combination Cracking and Treating
XIII—Treating Cracking Products
XIV—By-Products of Cracking
XV—Cracking Equipment
XVI—Reviews of Cracking

TRADE ANNOUNCEMENTS

New Du Pont Fabric

A new material making possible non-tarnishable metallic fabrics is announced by the Fabrics and Finishes Department of *E. I. du Pont de Nemours & Company*, Wilmington, Delaware. It is made of metallized slit cellulose film, and is manufactured by depositing a non-tarnishable metallic finish on one side of a sheet of Cellophane. Two such sheets are then laminated together, so that each side is metallic coated, and added strength is given to the stock. This sheet is then slit to narrow yarn widths, which then may be woven into a fabric in this form with rayon, silk, wool, or cotton. This material is the latest contribution of the chemical industry to the textile world. It is claimed for it that it will not tarnish or oxidize, thus solving a problem which has always proved difficult in the production of metallic textiles, of which there has been such a great vogue recently.

The new material was designed primarily for decorative use but its adaptation to other purposes has been so satisfactory that it is being employed also in the fashion field.

After many tests, it has been found to have a place also in the industrial field. It is adaptable to commercial methods of decorating such as lithographing, silk screen stenciling, embossing, corrugating, creping, shredding, and other methods of decoration used in making ribbons, gift ties, window backgrounds, wall coverings, and display mediums.

New Pyrene Pressure Extinguisher

Ruggedly constructed of copper and brass, this extinguisher has an inner seamless shell holding air under pressure and an outer shell containing Pyrene fire-extinguishing liquid. To keep both weight and cost low, no built-in pump is used, the air pressure being renewable from any air line producing 100 pounds pressure. The time-tested needle valve and not the tire valve retains the pressure. All operating parts are on the *outside*—easily accessible. It is compact—5″ diameter, 18″ high. And light—16½ pounds fully charged; 18 pounds shipping weight.

The Pyrene 2-quart pressure type fire extinguisher is approved by Underwriters' Laboratories for use wherever suitable air pressure is available. It is sold completely charged and with wall bracket, screws, and recharge date tag. A special bracket for use on vehicles is available at extra cost.

Further information upon request from *Pyrene Manufacturing Co.*, Newark, N. J.

"The Ring Method for Surface and Interfacial Tensions"

Above is the title of Bulletin No. 101 of the Technical Literature Series issued by the *Central Scientific Co.* Mimeographed, on standard letter-size sheets, in paper binder, 20 pp.; 6 cuts of apparatus on inserted pages. Excellent résumé of theory and practice. Many literature references, including a bibliography of bibliographies.

Reagents for Chemical Microscopy

A folder recently issued by *R. P. Cargille*, 118 Liberty St., New York City, describes the Shillaber Models of reagent sets for use in chemical microscopy. Set No. 1 is designed for use with Volume I, and Set No. 2 for use with Volume II of the "Handbook of Chemical Microscopy" by Chamot and Mason.

Celite Booklet

In a booklet entitled "After 50,000 Centuries—Research Puts the Diatom to Work," Dr. A. B. Cummins of the Johns-Manville Celite Research Laboratory tells the story of this minute but important organism. The life history of the diatom, research on diatomaceous earths, and industrial uses are discussed. 23 pp., 15.5 × 23 cm. *Johns-Manville*, 22 East 40th St., New York City.

Laboratory Stirrer

A new laboratory stirrer recommended as a sturdy, well-built accessory most useful for making emulsions; dissolving dyes, gums and resins, waxes and bitumens, pyroxylin, cellulose ethers, casein, glue, gelatin, starch, salts; extracting crude drugs and herbs, oil seeds, complex organic materials, etc., has been announced by the *Chemical Publishing Co. of N. Y., Inc.*, 175 Fifth Avenue, New York, N. Y.

Actuated by a shaded pole type motor (110 v., 60 cycle) it will run 24 hours daily without damage. It is non-sparking and will not be injured by fumes and vapors. The speed may be varied as needed by the rheostat. It fits an ordinary clamp holder or may be screwed to a shelf or wall. The shaft and propeller are furnished in chromium plate or Monel. A flexible, 6-foot rubber covered cord and soft rubber plug are included.

Gaertner Publications

The Gaertner Scientific Corporation, 1201 Wrightwood Ave., Chicago, has recently issued the following bulletins:

#134. "Spectrophotometer Assemblies," 8 pp., 19 × 26.5 cm.
#135. "Michelson Interferometer," 4 pp., 19 × 26.5 cm.
#136. "Comparators of Recent Design," 8 pp., 19 × 26.5 cm.

New Bausch & Lomb Publications

"The Surface Illuminator," 4 pp., 15.5 × 23.5 cm.

"The Ortho-stereo Camera and Ortho-stereoscope," 6 pp., 15.5 × 23.5 cm.

"Ajax-Northrup Electric Furnaces"

Bulletin No. 9 of *The Ajax Electrothermic Corporation*, Ajax Park, Trenton, N. J., describes various styles and sizes of small laboratory furnaces, as well as accessory apparatus. 4 pp., 21.5 × 28 cm.

Zinc Alloy Die Castings

The New Jersey Zinc Sales Co., 160 Front St., New York, has just published two booklets on zinc alloy die castings:

1. "A Visual Report of Progress—Zinc Alloy Die Castings," 80 pp., 21.5 × 28 cm., attempts by the use of 144 photographs to picture the complete scope of die-casting applications, to demonstrate the design and engineering advantages of zinc alloy die castings.

2. "Zamak Alloys for Zinc Alloy Die Castings," 42 pp., 21.5 × 28 cm., is a research bulletin on the four die-casting alloys developed and patented by this company. Since alloys of this type are almost universally used for present-day zinc alloy die castings, the technical data in this book will be of value to every design engineer.

Hammer Offset Film and Plates

A pamphlet (23 pp., 10 × 17.5 cm.), issued by the *Hammer Dry Plate Co.*, Saint Louis, Missouri, describing the offset process and manipulations. Formulas for development, fixation, dot etching, reduction, and intensification solutions are given.

Automatic, Magnetic Polishing Machine

E. Leitz, Inc., New York City, announces an improved type of "Guthrie-Leitz" machine for the polishing of metallurgical specimens. The new Model D is a material departure from the former model. It is described in Bulletin No. 21.